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(54) PRODUCTION OF COPOLYMER

(57) Abstract:

PURPOSE: To obtain a thermoplastic block copolymer resin excellent in impact resistance and mechanical strengths.
CONSTITUTION: A block copolymer is produced by using a silane having at least two Si-H bonds or a polyorganohydrogensiloxane having at least two Si-H bonds to combine an arom. vinyl polymer having unsatd. bonds at the molecular terminals and obtd. using an anionic polymn. initiator of the formula: $\text{CH}_2=\text{CH}-\text{R}_1-\text{M}$ (wherein R_1 is a 3-20C hydrocarbon group; and M is an alkali metal) with an olefin polymer having unsatd. bonds at the molecular terminals.

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CLAIMS

[Claim(s)]

[Claim 1] The manufacture approach of the block copolymer characterized by making it join together using the polyorgano hydrogen siloxane which has the silane or two or more Si-H association which have two or more Si-H association for a following component (a) and a following component (b).

(a) The following general formula (I)

$\text{CH}_2=\text{CH-R1}-\text{M (I)}$

It is the olefin system polymer which has an unsaturated bond at the aromatic series vinyl compound (polymer b) chain end which is obtained using the anionic initiator shown by (R1 expresses the hydrocarbon group of carbon numbers 3-20 among a formula, and M expresses an alkali-metal atom), and which has an unsaturated bond at the chain end.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of a block copolymer of combining the aromatic series vinyl compound polymer which has an unsaturated bond at the chain end, and the olefin system polymer which has an unsaturated bond at the chain end.

[0002] The block copolymer obtained by this is also the outstanding compatibilizer of polyphenylene ether, polyolefine or polyolefine, and high impact polystyrene at the outstanding modifier list to polyolefine, polystyrene, or polyphenylene ether while being thermoplastics which has the shock resistance excellent in itself.

[0003]

[Description of the Prior Art] the homopolymer of an alpha olefin (ethylene shall be included in this invention) or its copolymer is cheap -- in addition, since it has the outstanding mechanical strength, gloss, transparency, a moldability, moisture resistance, and chemical resistance, it is independent or is used widely as a polymer blend component. However, since the molecular structure is a non-polarity, an alpha olefin polymer is lacking in compatibility with others and the matter, and an adhesive property, printing nature, or the compatibility in a polymer blend is remarkably inferior in it.

[0004] In order to improve this, many methods of carrying out the graft polymerization of the

monomer in which a radical polymerization is possible to an alpha olefin polymer, and manufacturing a denaturation polymer have been tried for many years.

[0005] However, generally, a radical graft polymerization method has neither a rate of a graft, nor fully high graft efficiency, and since radical polymerization initiators, such as organic or an inorganic peroxide, are used in many cases, it has many problems – it is easy to produce molecule cutting and crosslinking reaction of a trunk polymer by which graft polymerization should be carried out.

[0006] Various proposals are made for the purpose of solving such a point. For example, suppressing molecule cutting and bridge formation of a trunk polymer in JP,57-98508,A and JP,2-269110,A each official report, and raising the rate of a graft of a monomer to it using the reactivity of the unsaturated bond of the copolymer of an alpha olefin and a nonconjugated diene monomer, is indicated.

[0007] However, this partial saturation copolymer is a nonconjugated diene monomer copolymeric is not necessarily high, and it is further hard to say that the radical graft reaction to this partial saturation copolymer is not necessarily practically completed in viewpoints, such as molecule cutting of the rate of a graft of a monomer, graft efficiency, or a trunk polymer.

[0008] Moreover, chain end double bond HEHAROGEN of the polyolefine obtained by Kaminsky mold Ziegler-Natta catalyst is made to add as approaches other than a radical graft polymerization method, and the method (JP,62-158709,A) of obtaining the block copolymer of an alpha olefin and styrene by the coupling reaction of it and living polystyryl-lithium is learned.

[0009] However, since an unreacted halogen remains in the manufactured copolymer, if this approach carries out melting kneading like extrusion molding or injection molding, coloring and degradation of a copolymer will tend to take place.

[0010] Furthermore, the method (JP,60-20918,A, Eur.Polym.J.17, 1175, 1981, Makromol.Chem.181, 1815, and 1980) of obtaining a block copolymer with polyolefine, polystyrene, or PORUBUTA diene is also learned by the so-called active-spot transformation method of the anionic polymerization active spot and the Ziegler Natta mold polymerization active spot.

[0011] However, these approaches have various troubles, like it is difficult to obtain the decline in the block copolymerization effectiveness by the thing with low (about 10%) active-spot conversion efficiency, and the controlled copolymer of molecular weight which is made into the purpose.

[0012] Moreover, although the method (JP,5-39331,A) of obtaining a block copolymer from the alpha olefin polymer and anionic polymerization nature monomer which have an unsaturated bond at the chain end is also learned, on the conditions in which anionic polymerization is possible, polyolefine needs to melt into a polymerization solvent and the molecular weight and the stereoregularity of polyolefine which can be used are restricted.

[0013]

[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned trouble and it aims at offering the manufacture approach of a copolymer of there not being molecule cutting or generating of gelation, and having high copolymerization effectiveness.

[0014]

[Means for Solving the Problem] This invention is the manufacture approach of the block copolymer characterized by combining the silane or Si-H coupling which has two or more Si-H coupling for a following component (a) and a following component (b) using the polyorgano hydrogen siloxane which it has two or more pieces.

[0015] (a) The following general formula (I)

[0016]

$\text{CH}_2=\text{CH-R}_1-\text{M}$ (I)

[0017] (R_1 expresses the hydrocarbon group of carbon numbers 3-20 among a formula, and M expresses an alkali-metal atom)

[0018] The aromatic series vinyl compound polymer which comes out and is obtained using the anionic initiator shown and which has an unsaturated bond at the chain end [0019] (b) The olefin system polymer which has an unsaturated bond at the chain end [0020] Hereafter, this invention is explained to a detail.

[0021] The anionic initiator used by <component (a)> (1) anionic-initiator this invention is a compound shown by the general formula (I).

[0022]

$\text{CH}_2=\text{CH-R}_1-\text{M}$ (I)

[0023] (R_1 expresses the hydrocarbon group of carbon numbers 3-20 among a formula, and M expresses an alkali-metal atom)

[0024] an upper type -- setting -- R_1 a carbon number -- desirable -- 3-15 -- it is 3-10 more preferably.

[0025] As an example of M, alkali-metal atoms, such as a lithium, sodium, and a potassium, are mentioned, among these it is a lithium atom preferably.

[0026] Although not limited, especially the synthetic approach of the above-mentioned anionic initiator (I) can make the compound and alkali metal which are usually shown by the following general formula (II) able to react, and can be acquired.

[0027]

$\text{CH}_2=\text{CH-R}_1-\text{X}$ (II)

[0028] (R_1 expresses the hydrocarbon group of carbon numbers 3-20 among a formula, and X expresses a halogen atom)

[0029] As an example of this anionic initiator (I), although 4-pentenyl lithium, 5-HECHISE nil lithium, 7-OKUTE nil lithium, 4-pentenyl sodium, 5-hexenyl sodium, 4-pentenyl potassium, a 5-hexenyl potassium, etc. are mentioned, a desirable thing is 4-pentenyl lithium.

[0030] (2) As an example of an aromatic series vinyl compound aromatic series vinyl compound, for example, styrene, alpha methyl styrene, alpha-methoxy styrene, methyl styrene, dimethyl styrene, 2 and 4, 6-trimethyl styrene, chloro styrene, dichloro styrene, bromostyrene, nitro styrene, chloromethyl styrene, cyano styrene, t-butyl styrene, vinyl naphthalene, etc. are mentioned, and styrene, alpha methyl styrene, and methyl styrene are desirable especially. these are independent -- or two or more sorts can be used together and it can use.

[0031] Moreover, in the range which does not exceed 50-mol %, copolymerization of these aromatic series vinyl compound and the copolymerizable monomer may be carried out, and they may be used. Copolymerization of these monomers may be carried out with which gestalten, such as random or a block. As these examples, they are a butadiene, an isoprene, methacrylic ester, hexamethyl cyclotrisiloxane, etc.

[0032] (3) -100-200 degrees C of -90-150 degrees C of conditions which carry out the polymerization of the aromatic series vinyl compound to a chain end using the manufacture above-mentioned anionic initiator (I) of an aromatic series vinyl compound polymer (a) which has an unsaturated bond can be more preferably performed under ordinary pressure, reduced pressure, or pressurization at the temperature of -80-100 degrees C.

[0033] as a solvent which can be used in the above-mentioned polymerization, aprotic polar-

solvents [, such as aromatic hydrocarbon; TERATO hydronalium furans, such as alicyclic hydrocarbon; benzene such as aliphatic hydrocarbon; cyclohexanes, such as n-hexane and n-heptane and decahydronaphthalene, toluene, o-, m-, or para xylene, dioxane, ethyl ether, a pyridine and a jig rim.]; etc. can be used, for example. These solvents may be independent or mixture is sufficient as them.

[0034] the number average molecular weight (henceforth "Mn") generally according to gel-permeation-chromatography (henceforth "GPC") measurement although the molecular weight of the aromatic series vinyl compound polymer (a) which has an unsaturated bond at this chain end is arbitrary -- 500-1,000,000 -- desirable -- 500-500,000 -- it is 1,000-100,000 more preferably.

[0035] The olefin system polymers which have an unsaturated bond at the chain end of the component (b) used by <component (b)> (1) alpha-olefin this invention are carbon numbers 2-12 and a copolymer which makes a principal component preferably the homopolymer of the alpha olefin of 2-8, or them. As an example of these alpha olefins, ethylene, a propylene, 1-butene, 1-hexene, a 3-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, 3, and 3-dimethyl-1-butene, 4, and 4-dimethyl-1-pentene, A 3-methyl-1-hexene, 4-methyl-1-hexene, 4, and 4-dimethyl-1-hexene, A 5-methyl-1-hexene, an allyl compound cyclopentane, an allyl compound cyclohexane, allyl compound benzene, a 3-cyclohexyl-1-butene, a vinyl cyclopropane, a vinyl cyclohexane, a 2-vinyl bicyclo [2.2.1]-heptane, etc. can be mentioned. As an example desirable [among these], ethylene, a propylene, 1-butene, 1-hexene, a 3-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, a 3-methyl-1-hexene, etc. can be mentioned, and ethylene, a propylene, 1-butene, 1-hexene, a 3-methyl-1-butene, or 4-methyl-1-pentene is especially desirable. The number of these alpha olefins one, and even if it uses two or more kinds, they do not interfere. When using two or more sorts of alpha olefins, these alpha olefins may be distributed at random in a partial saturation polymer, or it may be distributed in block.

[0036] (2) The olefin system polymer (b) which has an unsaturated bond at the chain end used for a chain end by manufacture this invention of the olefin system polymer (b) which has an unsaturated bond can be manufactured by two sorts of following approaches.

[0037] ** The approach of carrying out copolymerization of the above-mentioned alpha olefin, and alpha and omega-diene using a Ziegler-Natta catalyst. in this case -- although 1, 9-deca diene, 1, 13-tetra-deca diene, a divinylbenzene, etc. are mentioned and especially a limit does not have the amount of copolymerization of such dienes as an example of alpha to be used and omega-diene -- 0.01-30-mol % -- it is 0.05-20-mol % preferably. Less than [0.01 mol %], a block-copolymer yield becomes low at joint reaction time with a component (a), and if 30-mol % is exceeded, it will be easy to generate gelation etc. at the time of alpha olefin, alpha, and omega-diene copolymerization. Even if these alpha and omega-diene use two or more kinds even when they are independent or, they do not interfere.

[0038] ** The approach of carrying out the polymerization of the above-mentioned alpha olefin using the catalyst which consists of the following component (i) and (ii).

(i) A component (i) is a periodic table IVB-VIB group transition-metals compound which has at least one conjugated five-membered ring ligand. Specifically, it is shown by the following general formula (III) or the general formula (IV).

[0039]

Qa [C5 H5-a-b(R2) b] and [C5 H5-a-c(R3) c] MeXY (III) [0040]

Sa [C5 H5-a-d(R4) d] ZMeXY (IV)

[0041] Here, Q expresses the affinity radical which constructs a bridge in two conjugated five-membered ring ligands, and S expresses a conjugated five-membered ring ligand and the affinity

radical which constructs a bridge in Z sets. Specifically, it is [0042]. (b) Low-grade alkylene, its low-grade alkyl, or a phenyl permutation derivative, Preferably Methylene, ethylene, an isopropanol pyrene, phenylmethyl methylene, (b) silylenes, such as diphenylmethylene and cyclohexylene, thru/or oligo silylene, or the low-grade alkyl or a phenyl permutation derivative -- desirable -- silylene -- Dimethylsilylene, phenylmethyl silylene, diphenyl silylene, Germanium (Ha), such as disilylene and tetramethyl disilylene, Lynn, On the hydrocarbon-group (concrete target (CH3) containing nitrogen, boron, or aluminum, 2 germanium, (C six H5) 2germanium, P (CH3), P (C six H5), N (C four H9), N (C six H5), B (CH3), B (C four H9), B (C six H5), aluminum (C six H5), aluminum (CH3 O), etc. are] etc. In these, they are an alkylene group or a silylene radical preferably. a is 0 or 1.

[0043] Also although the conjugated five-membered ring ligand expressed with [C5 H5-a-b(R2) b], [C5 H5-a-c(R3) c], or [C5 H5-a-d(R4) d] is separately defined in the above-mentioned general formula, respectively It is R2 and R3 to b, c and d, and a list. And R4 Since the definition itself is the same (detail postscript), it cannot be overemphasized that you may differ even if these three conjugated five-membered ring radicals are the same.

[0044] One example of this conjugated five-membered ring radical is the cyclopentadienyl group (there are no substituents other than the bridge formation radicals Q and S) of $b=0$ ($c=0$ or $d=0$). Although one example of R2 (R3 or R4) is a hydrocarbon group (C1 - C20, preferably C1 - C12) when this conjugated five-membered ring radical is $b!=0$ ($c!=0$ or $d!=0$) and is what has a substituent Even if it has combined this hydrocarbon group with the cyclopentadienyl group as a univalent radical Moreover, when two or more these exists, the two pieces may join mutually together by each other end, and may form the condensed ring of a ring, i.e., a cyclopentadiene ring, with a part of cyclopentadienyl group concerned. That in which R2 (R3 or R4) shares the double bond of the cyclopentadienyl group concerned, and the latter example of representation forms the condensation six membered ring, i.e., this conjugated five-membered ring radical, is an indenyl group or a fluorenyl group. That is, the example of representation of this conjugated five-membered ring radical is a permutation or an unsubstituted cyclopentadienyl group, an indenyl group, or a fluorenyl group.

[0045] R2 and R3 And R4 C1 of the above respectively - C20 -- desirable -- the outside of the hydrocarbon group of C1 - C12 -- a halogen atom -- [-- for example fluorine, chlorine, and bromine), an alkoxy group (for example, thing of C1 - C12), and a silicon content hydrocarbon group -- [-- for example silicon -- an atom - Si -- (- R -) (R') (R'') -- a form -- containing -- a carbon number -- one - 24 -- about -- a radical --] - Lynn -- content -- a hydrocarbon group -- [- for example Lynn -- an atom - P -- (- R -) -- (- R - ' -) -- a form -- containing -- a carbon number -- one - 18 -- about -- a radical --] -- nitrogen -- content -- a hydrocarbon group -- [- for example nitrogen -- an atom - N -- (- R -) -- (- R - ' -) -- a form -- containing -- a carbon number -- one - 18 -- about -- a radical --] -- or -- boron -- content -- a hydrocarbon group -- [- for example, -- boron -- an atom - B -- (- R -) -- (- R - ' -) -- a form -- containing -- a carbon number -- one - 18 -- about -- a radical --] -- it is . b (c or d) is two or more, and when two or more R2 (R3 or R4) exists, even if they are the same, they may differ.

[0046] b, c, and d express the integer with which are satisfied of $0<=b<=4$, $0<=c<=4$, and $0<=d<=4$, when a is 0 and a is 1 about $0<=b<=5$, $0<=c<=5$, and $0<=d<=5$.

[0047] Me -- periodic-table IVB-VIB group transition metals -- they are titanium, a zirconium, or a hafnium preferably. It is a zirconium especially preferably.

[0048] Z -- oxygen (-O-), sulfur (-S-), and carbon numbers 1-20 -- desirable -- the alkoxy group of 1-10, and carbon numbers 1-20 -- desirable -- the thio alkoxy group of 1-12, and carbon

numbers 1-40 -- desirable -- the silicon content hydrocarbon group of 1-18, and carbon numbers 1-40 -- desirable -- the nitrogen content hydrocarbon group of 1-18, and carbon numbers 1-40 -- it is the Lynn content hydrocarbon group of 1-18 preferably. A part of Z sets have combined with S sets which are affinity radicals at the time of a= 1.

[0049] X and Y -- the each hydrogen atom; halogen atom; carbon numbers 1-20 -- desirable -- the hydrocarbon-group; carbon numbers 1-20 of 1-10 -- desirable -- the alkoxyl group; amino-group; carbon numbers 1-20 of 1-10 -- desirable -- Lynn content hydrocarbon-group [of 1-12] (specifically for example, diphenylphosphine radical);, or carbon numbers 1-20 -- desirable -- the silicon content hydrocarbon group of 1-12 -- [-- specifically, it is trimethylsilyl radical and bis(trimethylsilyl) methyl group]. Even if X and Y are the same, they may differ. A halogen atom and a hydrocarbon group are [among these] desirable.

[0050] The example of this transition-metals compound in case Me is a zirconium is as follows.

[0051] (b) The transition metals which do not have the joint radical which constructs a bridge but have two conjugated five-membered ring ligands, for example, [0052]

Bis(cyclopentadienyl)zirconiumdichloride, bis(methylcyclopentadienyl)zirconiumdichloride, bis(dimethylcyclopentadienyl)zirconiumdichloride, bis(trimethylcyclopentadienyl)zirconiumdichloride, bis(tetramethylcyclopentadienyl) zirconium dichloride, [0053] Bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl) zirconium dichloride, bis(indenyl)zirconiumdichloride, bis(fluorenyl) zirconium dichloride, a bis(cyclopentadienyl) zirconium monochrome RIDOMONO hydride, [0054] Bis(cyclopentadienyl) methyl zirconium mono-chloride, bis(cyclopentadienyl) ethyl zirconium mono-chloride, bis(cyclopentadienyl) phenyl zirconium mono-chloride, bis(cyclopentadienyl) zirconium dimethyl, bis(cyclopentadienyl) zirconium diphenyl, [0055] Bis(cyclopentadienyl)zirconiumdineopentyl, bis(cyclopentadienyl) zirconium JIHAIDORAIDO, zirconium dichloride (indenyl (cyclopentadienyl)), zirconium dichloride (fluorenyl (cyclopentadienyl)), etc.

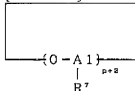
[0056] (b) The transition-metals compound which has two five-membered ring ligands which constructed the bridge by the alkylene group, for example, [0057] Methylenebis (indenyl) zirconium dichloride, ethylene bis(indenyl)zirconiumdichloride, ethylene bis(indenyl) zirconium mono-hydride monochloride, ethylene bis(indenyl) methyl zirconium mono-chloride, ethylene bis(indenyl) zirconium mono-methoxide MONOKURORIDO, [0058] Ethylene bis(indenyl) zirconium JIETOKISHIDO, ethylene bis(indenyl) zirconium dimethyl, ethylene bis(4, 5, 6, 7-tetrahydroindenyl) zirconium dichloride, ethylene bis(2-methyl indenyl) zirconium dichloride, ethylene bis(2-ethyl indenyl) zirconium dichloride, [0059] Ethylene bis(2, 4-dimethyl indenyl) zirconium dichloride, Ethylene (2, 4-dimethylcyclopentadienyl) (3', 5'-dimethylcyclopentadienyl) zirconium dichloride, Ethylene (2-methyl-4-tert-butyl-cyclopentadienyl) (3'-tert-butyl-5'-methylcyclopentadienyl) zirconium dichloride, Ethylene (2, 3, 5-trimethylcyclopentadienyl) (2', 4', 5'-trimethylcyclopentadienyl) zirconium dichloride, isopropylidene bis(indenyl)zirconiumdichloride, [0060] Isopropylidene (2, 4-dimethylcyclopentadienyl) (3', 5'-dimethylcyclopentadienyl) zirconium dichloride, Isopropylidene (2-methyl-4-tert-butylcyclopentadienyl) (3'-tert-butyl-5'-methylcyclopentadienyl) zirconium dichloride, Methylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium dichloride, Methylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium chloride hydride, methylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium dimethyl, [0061] Methylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium diphenyl, Methylene (cyclopentadienyl) (trimethylcyclopentadienyl) zirconium dichloride, Methylene

(cyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride, Isopropylidene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium dichloride, isopropylidene (cyclopentadienyl) (2, 3, 4, 5-tetramethylcyclopentadienyl) zirconium dichloride, [0062] Isopropylidene (cyclopentadienyl) (3-methyl indenyl) zirconium dichloride, isopropylidene (cyclopentadienyl) (fluorenyl) zirconium dichloride, isopropylidene (2-methylcyclopentadienyl) (fluorenyl) zirconium dichloride, isopropylidene (2, 5-dimethylcyclopentadienyl) (3', 4'-dimethylcyclopentadienyl) zirconium dichloride, isopropylidene (2, 5-dimethylcyclopentadienyl) (fluorenyl) zirconium dichloride, [0063] Ethylene (cyclopentadienyl) (3, 5-dimethylcyclopentadienyl) zirconium dichloride, Ethylene (cyclopentadienyl) (fluorenyl) zirconium dichloride, Ethylene (2, 5-dimethylcyclopentadienyl) (fluorenyl) zirconium dichloride, Ethylene (2, 5-diethyl cyclopentadienyl) (fluorenyl) zirconium dichloride, Diphenylmethylene (cyclopentadienyl) (3, 4-diethyl cyclopentadienyl) zirconium dichloride, Cyclohexylidene (cyclopentadienyl) (fluorenyl) zirconium dichloride, cyclohexylidene (2, 5-dimethylcyclopentadienyl) (3', 4'-dimethylcyclopentadienyl) zirconium dichloride, etc.

[0064] (c) The transition-metals compound which has a silylene radical bridge formation five-membered ring ligand, for example, [0065] Dimethylsilylene bis(indenyl)zirconiumdichloride, dimethylsilylene bis(4, 5, 6, 7-tetrahydroindenyl) zirconium dichloride, dimethylsilylene bis(2-methyl indenyl) zirconium dichloride, dimethylsilylene bis(2, 4-dimethyl indenyl) zirconium dichloride, dimethylsilylene bis(2-methyl - 4, 5, 6, 7-tetrahydroindenyl) zirconium dichloride, [0066] Dimethylsilylene (2, 4-dimethylcyclopentadienyl) (3', 5'-dimethylcyclopentadienyl) zirconium dichloride, Phenylmethyl silylene bis(indenyl)zirconiumdichloride, Phenylmethyl silylene bis(4, 5, 6, 7-tetrahydroindenyl) zirconium dichloride, Phenylmethyl silylene (2, 4-dimethylcyclopentadienyl) (3', 5'-dimethylcyclopentadienyl) zirconium dichloride, Phenylmethyl silylene (2, 3, 5-trimethylcyclopentadienyl) (2', 4', 5-trimethylcyclopentadienyl) zirconium dichloride, [0067] Phenylmethyl silylene bis(tetramethylcyclopentadienyl) zirconium dichloride, diphenyl silylene bis(indenyl)zirconiumdichloride, tetramethyl disilylene bis(indenyl)zirconiumdichloride, tetramethyl disilylene bis(cyclopentadienyl)zirconiumdichloride, tetramethyl disilylene (3-methylcyclopentadienyl) (indenyl) zirconium dichloride, [0068] Dimethylsilylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium dichloride, Dimethylsilylene (cyclopentadienyl) (trimethylcyclopentadienyl) zirconium dichloride, Dimethylsilylene (cyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride, Dimethylsilylene (cyclopentadienyl) (3, 4-diethyl cyclopentadienyl) zirconium dichloride, dimethylsilylene (cyclopentadienyl) (triethyl cyclopentadienyl) zirconium dichloride, [0069] Dimethylsilylene (cyclopentadienyl) (tetraethyl cyclopentadienyl) zirconium dichloride, dimethylsilylene (cyclopentadienyl) (fluorenyl) zirconium dichloride, dimethylsilylene (cyclopentadienyl) (2, 7-G t-butyl fluorenyl) zirconium dichloride, dimethylsilylene (cyclopentadienyl) (octahydro fluorenyl) zirconium dichloride, dimethylsilylene (2-methylcyclopentadienyl) (fluorenyl) zirconium dichloride, [0070] Dimethylsilylene (2, 5-dimethylcyclopentadienyl) (fluorenyl) zirconium dichloride, Dimethylsilylene (2-ethylcyclopentadienyl) (fluorenyl) zirconium dichloride, Dimethylsilylene (2, 5-diethyl cyclopentadienyl) (fluorenyl) zirconium dichloride, Diethylsilylene (2-methylcyclopentadienyl) (2', 7'-G t-butyl fluorenyl) zirconium dichloride, Dimethylsilylene (2, 5-dimethylcyclopentadienyl) (2', 7'-G t-butyl fluorenyl) zirconium dichloride, [0071] Dimethylsilylene (2-ethylcyclopentadienyl) (2', 7'-G t-butyl fluorenyl) zirconium dichloride, Dimethylsilylene (diethyl cyclopentadienyl) (2', 7'-G t-butyl fluorenyl) zirconium dichloride, Dimethylsilylene (methylcyclopentadienyl) (octahydro fluorenyl) zirconium dichloride,

[0085]

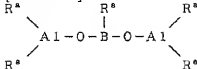
[Formula 2]



(VI)

[0086]

[Formula 3]



(VII)

[0087] (the inside of a formula, and p -- 0-40 -- desirable -- the integer of 2-30 -- it is -- R5, R6, and R7 and R8 -- an each hydrogen atom -- or -- desirable -- carbon numbers 1-10 -- the hydrocarbon group of carbon numbers 1-6 is expressed more preferably)

[0088] The compound of a general formula (V) and (VI) is a compound called alumoxane, and is a product obtained by the reaction of one kind of trialkylaluminum or two or more kinds of trialkylaluminums, and water. Specifically, the trialkylaluminum of one kind of (b), the methylalumoxane obtained from water, ethylalumoxane, propyl alumoxane, buthylalumoxane, isobuthylalumoxane, the trialkylaluminum of two kinds of (b)s and the methylethyl alumoxane obtained from water, methylbutyl alumoxane, methyl isobuthylalumoxane, etc. are illustrated. In these, especially a desirable thing is methyl ARUMOKISA or methyl isobuthylalumoxane.

[0089] These alumoxane can also be used [also using two or more sorts together by the inside of each group, and each between groups one, or] together with other alkylaluminum compounds, such as trimethylaluminum, triethylaluminum, triisobutylaluminum, and dimethyl aluminum chloride, possible.

[0090] These alumoxane can be prepared by well-known various approaches, and the following approaches are specifically illustrated.

[0091] (b) the approach to which trialkylaluminum makes react with direct water using suitable organic solvents, such as toluene, benzene, and the ether, and (***) -- the approach of mixing the approach and the (d) trimethylaluminum to which the hydrate of the salt hydrate which has trialkylaluminum and water of crystallization, for example, a copper sulfate, and an aluminum sulfate, the approach and the trialkylaluminum (Ha) made to react, and the moisture into which silica gel etc. be infiltrated be made to react, and triisobutylaluminum, and making it react with direct water using suitable organic solvents, such as toluene, benzene, and the ether, and [0092] (e) Mix trimethylaluminum and triisobutylaluminum. How to carry out a pyrogenetic reaction to hydrates, such as the salt hydrate which has water of crystallization, for example, a copper sulfate, and an aluminum sulfate, After infiltrating moisture into (**) silica gel etc. and processing by triisobutylaluminum, The approach, (g) methylalumoxane, and isobuthylalumoxane which carry out additional processing by trimethylaluminum are compounded by the well-known approach. How to put the salt which has water of crystallization, such as copper-sulfate 5 monohydrate, into aromatic hydrocarbon solvents, such as the approach of carrying out specified quantity mixing of the these 2 component, and carrying out a

pyrogenetic reaction, (h) benzene, and make it react with the about -40-40-degree C bottom trimethylaluminum of a temperature condition. In this case, the amounts of the water to be used are usually 0.5-1.5 in a mole ratio to trimethylaluminum. Thus, the obtained methylalumoxane is the polymer of linear or annular organic aluminium. [0093] The compound shown by the general formula (VII) is one kind of trialkylaluminium or two or more kinds of trialkylaluminiums, and the following general formula (VIII).

[0094]

R9 -B-(OH)₂ (VIII)

[0095] it can come out and can obtain by the reaction of the mole ratios 10:1-1:1 with the alkyl boron acid (the inside of a formula, and R9 -- carbon numbers 1-10 -- the ARUKI radical of carbon numbers 1-6 is expressed preferably) shown. concrete -- (**) -- trimethylaluminum, the reactant of 2:1 of a methyl boron acid, and (**) -- triisobutylaluminum, the reactant of 2:1 of a methyl boron acid and trimethylaluminum (Ha), triisobutylaluminum, the reactant of 1:1:1 of a methyl boron acid and (d) trimethylaluminum, the reactant of 2:1 of an ethyl boron acid, (e) triethylaluminum, the reactant of 2:1 of a butyl boron acid, etc. are illustrated. The compound of these general formulas (VII) is possible also for using two or more sorts, and can also be used together with other alkylaluminum compounds, such as alumoxane shown by the general formula (V) or (VI), and trimethylaluminum, triethylaluminum, triisobutylaluminum, dimethyl aluminum chloride.

[0096] Moreover, as an ionicity compound which it reacts with a component (i) and can change a component (i) into a cation, there are some which are shown by the general formula (IX).

[0097]

[K] e+[Z] e- (IX)

[0098] Here, K is the cation component of ionicity, for example, a carbonium cation, a tropylium cation, an ARUMONIUMU cation, an oxonium cation, a sulfonium cation, a HOSUFONIUMU cation, etc. are mentioned. Moreover, a metaled cation, a cation of an organic metal, etc. which itself is easy to be returned are mentioned. As an example of these cations, the (b) triphenyl carbonium, The diphenyl carbonium, cyclo hepta-TORIENIUMU, indie NIUMU, Triethyl ammonium, TORIPURO pill ammonium, tributyl ammonium, N and N-dimethyl anilinium, dipropyl ammonium, dicyclohexyl ammonium, Triphenyl phosphonium, trimethyl phosphonium, the Tori (dimethylphenyl) phosphonium, There are the Tori (methylphenyl) phosphonium, triphenylsulfonium, triphenyl oxonium, triethyl oxonium, kinky thread RIUMU and complex ion, golden ion, platinum ion, a copper ion, palladium ion, mercury ion, ferro SENIUMU ion, etc.

[0099] Z in the above-mentioned general formula (IX) is the anion component of ionicity, and it is the component (generally non-coordination) which serves as an opposite anion to the cation kind from which the component (i) was changed, for example, an organic boron compound anion, an organoaluminium compound anion, an organic gallium compound anion, an organic phosphorous compound anion, an organic arsenical compound anion, an organic-antimony-compounds anion, etc. are mentioned. concrete -- (**) -- tetra-phenyl boron and tetrakis (3, 4, 5-trifluoro phenyl) boron -- Tetrakis (3, 5-JI (trifluoromethyl) phenyl) boron, Tetrakis (3, 5-JI (t-butyl) phenyl) boron, tetrakis (pentafluorophenyl) boron, (**) -- tetra-phenyl aluminum and tetrakis (3, 4, 5-truffe ROORO phenyl) aluminum -- Tetrakis [3 and 5-JI (trifluoromethyl) phenyl] aluminum, Tetrakis [3 and 5-JI (t-butyl) phenyl] aluminum, tetrakis (pentafluorophenyl) aluminum, A tetra-phenyl gallium, a tetrakis (3, 4, 5-trifluoro phenyl) gallium, (Ha) A tetrakis [3 and 5-JI (trifluoromethyl) phenyl] gallium, A tetrakis [3 and 5-JI (t-butyl) phenyl] gallium, a

tetrakis (pentafluorophenyl) gallium, (**) -- tetra-phenyl phosphorus and tetrakis (pentafluorophenyl) Lynn -- (**) -- tetra-FENIRUHI -- base and a tetrakis (pentafluorophenyl) arsenic -- (**) -- tetra-phenyl antimony, tetrakis (pentafluorophenyl) antimony, (g) deca borate, undeca borate, KARUBA dodeca borate, deca chloro deca borate, etc. are illustrated.

[0100] Moreover, if Lewis acid, especially a component (i) are used as Lewis acid convertible into a cation, various organic boron compounds, a metal halogenated compound, or solid acid is illustrated. concrete -- (**) -- triphenyl boron and tris (3, 5-difluoro phenyl) boron -- Organic boron compounds, such as tris (pentafluorophenyl) boron; A (b) aluminum chloride, The aluminium bromide, an aluminium iodide, a magnesium chloride, a magnesium bromide, Magnesium iodide, bromine chloride magnesium, chlorination magnesium iodide, bromination -- magnesium iodide, a magnesium chloride hydride, and magnesium chloride hydronalium oxide - - magnesium bromide hydronalium oxide, chlorination magnesium alkoxide, and bromination -- solid acid, such as metal halogenated compound [, such as magnesium alkoxide,]; or (Ha) a silica alumina, and an alumina, etc. is mentioned.

[0101] these ionicity compounds and Lewis acid -- as a component (ii) -- independent -- it can also use -- a general formula (V) and (VI) -- or (VII) can be used together with an aluminum oxy compound. Moreover, it is also possible to use together with organoaluminium compounds, such as trimethylaluminum, triethylaluminum, triisobutylaluminum, a diethyl aluminum phenoxide, and dimethyl aluminum chloride, as trialkylaluminium and dialkyl aluminum mono-halide, monoalkyl aluminum dihalide and alkylaluminium sesquihalide, the things that a part of these alkyl groups replaced with the list with the phenoxy group, and these examples.

[0102] (iii) The desirable catalyst of this invention can be acquired by making the bottom of existence of the monomer to which it is in a polymerization tank or the polymerization of an above-mentioned component (i) and an above-mentioned component (ii) should be carried out out of a polymerization tank, or nonexistence contact.

[0103] The amount of the component (i) used by this invention and the component (ii) used is arbitrary. For example, in the case of a solvent polymerization, the amount of the component (i) used is 10-7-102 as a transition-metals atom. Within the limits of millimol/liter, and 10-4 - 1 millimol / liter is more desirable. In the case of an aluminum oxy compound, as for the mole ratio of aluminum/transition metals, 10-100,000, and 100-20,000 are usually desirable, and its range of 100-10,000 is more desirable. the case where an ionicity compound or Lewis acid is used as a component (ii) on the other hand -- the mole ratio of opposite transition metals -- 0.1-1,000 -- desirable -- 0.5-100 -- it is more preferably used in 1-50.

[0104] Although it is as having described above that the catalyst of this invention is what may contain other components in addition to a component (i) and (ii) As the third component (arbitration component) which can be added to a component (i) and (ii) For example, active hydrogen content compounds, such as H₂ O, a methanol, ethanol, and a butanol; The ether, Electron-donative compounds, such as ester and an amine; alkoxy content compounds, such as boric-acid phenyl, dimethyl methoxy aluminum, phosphorous acid phenyl, a tetra-ethoxy silane, and diphenyldimethoxysilane, etc. are mentioned.

[0105] The manufacture approach of the block copolymer in <manufacture of block copolymer> this invention is combining a component (a) and a component (b) by hydrosilylation, and should just have Si-H association in [two or more] 1 molecule as the silane used for hydrosilylation, or a polyorgano hydrogen siloxane.

[0106] As an example of such a silane or a polyorgano hide JIEN siloxane, diethylsilane, phenylsilane, a methylphenyl silane, poly methylhydrogensiloxane, a polyphenyl hydrogen

siloxane, etc. are mentioned.

[0107] A reaction condition is -50-200 degrees C in temperature, and can be made to react under ordinary pressure, reduced pressure, or pressurization preferably -100-300 degrees C.

[0108] As a reaction solvent, although an aliphatic hydrocarbon solvent, an alicyclic hydrocarbon solvent, an aromatic hydrocarbon solvent, an aprotic polar solvent, etc. can be used, for example, what may dissolve a component (a) and (b) with both reaction temperature is desirable.

[0109] Moreover, the catalyst for promoting a reaction as occasion demands may be used. As a catalyst, transition-metals compounds, such as Pt, Rh, Pd, and nickel, are usually used. Chloroplatinic acid (H_2PtCl_6) etc. is mentioned as these examples.

[0110] Reaction time can be set as arbitration by various reaction conditions.

[0111] When the usual application offers the block copolymer obtained by this invention, in this copolymer, an unreacted component (a) and an unreacted component (b) may be included.

[0112]

[Example] Although an example is given to below and this invention is concretely explained to it, this invention is not limited to these.

[0113] The following manufactures were performed under the manufacture high vacuum of an example of reference 1: 4-pentenyl lithium using the breaking seal method. Namely, metal lithium 5g And 5-BUROMO-1-pentene 6g It was made to react for three days at a room temperature in addition to n-heptane 120ml. Next, diethylether 40ml was added to this reaction mixture, the churning back fault was carried out at 0 degree C for 24 hours, and the solvent of the filtrate was distilled off. It was checked that the peak of a vinyl group and the methyl anion origin was observed, and 4-pentenyl lithium had been obtained by 1H -NMR analysis. Yield was 70%.

[0114] The example 2 of reference: It carried out to the end under the high vacuum using the breaking seal method like the example 1 of synthetic reference of the polystyrene which has an unsaturated bond. Namely, 4-pentenyl lithium 0.08g obtained in the example 1 of reference It dilutes with n-heptane 9.3ml and is styrene 6.2g about this. After being dropped at the bottom of churning in the solution which mixed benzene 200ml and carrying out a polymerization at a room temperature for 2 hours, methanol 2ml was added and the polymerization was stopped. It is methanol 1L about this reaction mixture. It flowed into inside and the polymer which precipitated was dried the ** exception. the obtained polymer (henceforth "Resin A") -- 6.2g it is -- as a result of GPC measurement, M_n was 6,270 and weight average molecular weight (henceforth " M_w ") was 8,080. It was checked from the ratio of the peak intensity which originates in the peak intensity originating in the polystyrene principal chain of Resin A, and an end vinyl group by 1H -NMR analysis that the vinyl group is introduced into all the piece ends of a polymer.

[0115] The example 3 of reference: Set for the example 2 of synthetic reference of the polystyrene which has an unsaturated bond at the end, and it is 7.0g about the amount of 0.04g and styrene in the amount of 4-pentenyl lithium. It carried out like the example 2 of reference except having changed. the obtained polymer (henceforth "Resin B") -- 6.9g it is -- as a result of measurement of GPC, M_n was 14,400 and M_w was 15,600. That the vinyl group is altogether introduced also into the end of Resin B I understand from analysis of 1H -NMR.

[0116] example of reference 4: -- manufacture of synthetic (1) ethylene bis(indenyl)zirconiumdichloride of the polypropylene which has an unsaturated bond at the end - 300ml glass flask which fully carried out the nitrogen purge -- bis(indenyl) ethane 5.16g And

tetrahydrofuran 150ml was inserted in and it cooled to -78 degrees C. Butyl lithium (product made from Aldrich) 25ml (concentration of 1.6 mols/l.) is bet on this for 1 hour, and is dropped at it, and the temperature up was carried out gradually and it was made to flow back after that to reflux temperature for 2 hours.

[0117] On the other hand, a tetrahydrofuran is cooled to -78 degrees C after 100ml insertion in 200ml glass flask which fully carried out the nitrogen purge, and it is 4.7g of zirconium tetrachlorides to it. In addition, the temperature up was gradually carried out to the room temperature. Package addition of this zirconium tetrachloride solution was carried out at 0 degree C into the lithium salt solution of the above-mentioned bis(indenyl) zirconium, the temperature up was carried out to reflux temperature after that, and the reaction was continued at reflux temperature for 16 hours. The generated yellow solid-state was carried out the ** exception, the methanol washed, and it dried under reduced pressure. 1.9g Ethylene bis(indenyl)zirconiumdichloride was obtained.

[0118] (2) manufacture trimethylaluminum 48.2g of methylalumoxane 565ml of included toluene solutions -- the bottom of churning, and 50g of copper-sulfate 5 monohydrates 0 degree C -- 5g every -- it supplied at intervals of 5 minute. Carry out a temperature up to 25 degrees C slowly, and it is made to react at 25 degrees C for 2 hours, and the temperature up of the solution was carried out to 35 more degrees C, and it was made to react for two days after termination. The solid-state of the copper sulfate which remains was separated and the toluene solution of alumoxane was obtained. The concentration of methylalumoxane was 27.3mg (2.7w/v %)/ml.

[0119] (3) Content volume 1.0L equipped with the polymerization agitator and the temperature controller Toluene 400ml fully dehydrated and deoxidized, methylalumoxane 580mg, and ethylene bis(indenyl)zirconiumdichloride 0.418mg (0.001mmol) were introduced into the autoclave made from stainless steel, and the polymerization was carried out to it at propylene pressure 7kg/cm2G and 40 degrees C for 4 hours. It is 3L after polymerization termination and about a polymerization solution. It is 180g, when it extracts in a methanol, and the polymer was carried out the ** exception and dried. Resin (henceforth "Resin C") was collected. This thing was Mn18,700 and molecular weight distribution (Mw/Mn) 1.99 as a result of GPC measurement.

[0120] The [mm] molar fraction of TORIADDO was 0.888 as a result of 13 C-NMR (JEOL Co., Ltd. make, trade name: JEOL-FX-200) analysis, and all single-sided ends were vinylidene association (0.79 per 1,000 carbon atom).

[0121] The example 5 of reference: Except having changed polymerization temperature to 20 degrees C in the example 4 of synthetic reference of the polypropylene which has a partial saturation radical at the end, carry out like the example 4 of reference and it is 43g. Resin (henceforth "Resin D") was obtained. Mn of this thing was 32,500 and Mw/Mn was 1.93.

[0122] example of reference 6: -- manufacture of synthetic (I) solid-state catalyst component (i) of a propylene and the copolymer of 1 and 9-deca diene -- n-heptane 200ml dehydrated and deoxidized in the flask which fully carried out the nitrogen purge -- introducing -- subsequently - - MgCl2 0.4 mols and Ti (O-nC four H9)4 0.8 mols were introduced and it was made to react at 95 degrees C for 2 hours. Temperature was lowered to 40 degrees C after reaction termination, subsequently methyl hydronalium polysiloxane (thing of 20cS) 48ml was introduced, and it was made to react for 3 hours. The generated solid-state component was washed by n-heptane.

[0123] Subsequently, n-heptane 50ml refined like the above was introduced into the flask which fully carried out the nitrogen purge, and 0.24 mols of solid-state components compounded above were introduced by Mg atom conversion. Subsequently, the SiCl4 0.4 mol was mixed to n-

heptane 25ml, and it introduced to the flask in 30 degrees C and 30 minutes, and was made to react at 70 degrees C for 3 hours. It washed by n-heptane after reaction termination. Subsequently, 0.024 mols of phthalic-acid chloride were mixed to n-heptane 25ml, and it introduced to the flask in 70 degrees C and 30 minutes, and was made to react at 90 degrees C for 1 hour.

[0124] It washed by n-heptane after reaction termination. Subsequently, SiCl₄ 20ml was introduced and it was made to react at 80 degrees C for 6 hours. It fully washed by n-heptane after reaction termination. The titanium content of this component was 1.21 % of the weight.

[0125] the component which introduced 50ml of fully refined n-heptanes into the flask which fully carried out the nitrogen purge, and was subsequently obtained above -- 5g introducing -- subsequently (CH₃) -- 3 CSi (CH₃) (OCH₃)₂ [a component (ii)] -- 1.6ml -- introducing -- subsequently -- TiCl₄ 0.52ml -- further -- triethylaluminum 3.0g It introduced, respectively and was made to contact at 30 degrees C for 2 hours. It washed enough by n-heptane after contact termination, and considered as the solid-state component (i). The titanium content in a solid-state component (i) was 3.64 % of the weight.

[0126] Content volume 1.5L which fully carried out the nitrogen purge It is n-butyl lithium 0.4g as a component (ii) after introducing into a churning type autoclave n-heptane 400ml dehydrated and deoxidized and cooling the inside of a system at 15 degrees C. And above-mentioned solid-state (component i) 4g It introduced, feed of the propylene was carried out by 8g/hr for 0.5 hours, and precurving was performed. The residual-pressure polymerization was performed for 10 minutes after propylene feed termination. It washed twice by n-heptane after termination, and the target catalyst component for polymerizations was obtained. 4g of this catalyst component for polymerizations Upwards, a polymer is 3.72g. A **** and the solid-state catalyst component for polymerizations (i) are 7.72g. It was obtained.

[0127] (2) Manufacture inner capacity 10L of a copolymer n-heptane 2.5L after a propylene permutes an autoclave It teaches and is triethylaluminum 2.5g. And above-mentioned solid-state catalyst (component i) 0.4g It introduced into the bottom of a propylene ambient atmosphere.

[0128] Subsequently, the propylene was pressed fit agitating and it held for 10 minutes to 65 degrees C and 0.5kg/cm²G. Then, the charge of 1 and 9-deca diene was started and pressurization maintenance was carried out with the propylene at 2.0kg/cm²G at coincidence. 1 and 9-deca diene is 350 ml/hr. It inserted in for 2 hours. In addition, just before introducing the solid-state catalyst component (i), the time [from] of polymerization termination held the hydrogen concentration of the autoclave gaseous-phase section to 4.0 volume %. After inactivating a catalyst by the 5 hours after n-butanol, catalyst residue was extracted with water, centrifugal separation recovered the copolymer, and it dried.

[0129] The obtained copolymer (henceforth "Resin E") powder was 2.1kg, and bulk density was 0.51g/cc. As a result of GPC measurement, Mn was 56,000 and Mw was 350,000. Again The content of 1 and 9-deca diene in which copolymerization was carried out by analysis by 1 H-NMR was 0.33-mol %.

[0130] an example 1 -- 200ml flask which fully carried out the nitrogen purge -- resin C 1.3g and resin A Xylene 40ml fully dehydrated and deoxidized 1.3g and poly methylhydrogensiloxane (Shin-Etsu Chemical [Co., Ltd.] make trade name: KF99) 0.025g And platinum / divinyl tetramethyl disiloxane (Shin-Etsu Chemical Co., Ltd. make, trade name-L50T) 0.014g It put in and was made to react at 160 degrees C under nitrogen-gas-atmosphere mind for 144 hours.

[0131] Then, methanol 500ml is filled with a reaction solution, - desiccation classified by ** of the precipitating block copolymer is done, and it is 2.5g. It obtained.

[0132] 2g of this block copolymer - desiccation classified by ** of the block copolymer which added to methyl-ethyl-ketone 500ml, and precipitated to xylene 100ml after carrying out the heating dissolution was done. the collected block copolymer -- 1.9g it is -- the styrene content was 49.0 % of the weight by the infrared spectral-analysis method. This thing was Mn25,000 and Mw51,000 as a result of GPC measurement.

[0133] It sets in the example 2 example 1, and is Resin C. 0.65g, resin A 1.95g Except having changed, it carries out like this example and is 2.4g of block copolymers. It obtained.

[0134] the block copolymer collected as a result of performing purification processing and analysis like an example 1 -- 1.8g it is -- the styrene content was 60 % of the weight. Moreover, it was Mn29,000 and Mw66,000.

[0135] Except having changed Resin C to Resin D, and having changed Resin A to Resin B in example 3 example 1, it carries out like this example and is 2.5g of block copolymers. It collected.

[0136] the block copolymer collected as a result of performing purification processing and analysis like an example 1 -- 1.5g it is -- the styrene content was 31.1 % of the weight. Moreover, it was Mn53,600 and Mw108,000.

[0137] Except having changed Resin C to Resin E in example 4 example 1, it carries out like this example and is 2.5g of block copolymers. It collected.

[0138] the block copolymer collected as a result of performing purification processing and analysis like an example 1 -- 1.7g it is -- the styrene content was 38.8 % of the weight. Moreover, it was Mn63,000 and Mw360,000.

[0139] the example 1 of a comparison -- the inside of the round bottom flask which fully carried out the nitrogen purge -- resin C5g After having put in 200ml of carbon tetrachlorides, carrying out the temperature up to 70 degrees C and agitating for 30 minutes at this temperature, it cooled to the room temperature under churning. It is 0.18g of bromines there. After making it react for 1 hour, the temperature up was carried out to 60 degrees C, and it was made to react further for 30 minutes in addition.

[0140] Subsequently, it is methanol 2L about contents in a flask. It agitated [be / it / under adding] for 1 hour, and suction filtration was carried out and the solid-state product was carried out the ** exception. Furthermore, after repeating actuation of adding a solid-state product to a methanol and filtering it, 4 times, a solid-state product is dried, and it is 4.98g. The bromination polymer was obtained. As a result of measuring a bromine content with ion chromatography, it was 3.3 % of the weight.

[0141] In the flask, styrene 6.7g and xylene 115ml were added, n-butyl lithium 49mg was added there, and the living poly styryl anion was compounded.

[0142] It is the 1.0g of the above-mentioned bromination polymers into another flask. It put in, xylene 120ml was added and it agitated at 50 degrees C. Said living poly styryl anion is added there, and it agitated for 144 hours and was made to react at 50 degrees C.

[0143] Subsequently, this was poured in and settled into the methanol of an overlarge, and solid-state products were collected and it dried. After making 1,4-dioxane carry out the **** dissolution of this solid-state product for 2 hours and leaving it at 20 degrees C of night, the insoluble sections were collected the ** exception and it dried.

[0144] the obtained polymer -- 1.01g it is -- when the content of polystyrene was calculated from the infrared absorption spectrum, it was 6.5 % of the weight. Moreover, as a result of measuring a bromine content with ion chromatography, it was 1.5 % of the weight.

[0145] the block copolymer obtained in an application 1 and the two examples 1, polypropylene

(Mitsubishi Petrochemical Co., Ltd. make; trade name "MA8"), and Pori (2, the 6-dimethyl -1, 4-phenylene ether) (Japanese polyether company make --) Intrinsic viscosity measured in the chloroform in 30 degrees C: Use the PURASUTO mill (Oriental energy machine factory company make) of 60ml of content volume by the presentation shown in Table 1 by making 0.4 dl/g into an application 1, and they are for 5 minutes and rotational frequency 180rpm at 230 degrees C. Melting kneading was carried out. The following estimated physical properties for the obtained resin constituent, and the result was shown in Table 1. It was similarly shown in Table 1 by making into an application 2 (comparison) the case where a block copolymer is not used.

[0146] (1) Carry out cutting of the test piece with a bending elastic-modulus width of face [of 25mm], and a die length of 80mm, and it is JIS. K Based on 7203, it measured using the Instron testing machine.

[0147] (2) Injection molding of the test piece with Izod-impactive-strength die length of 31.5mm, a width of face [of 6.2mm], and a thickness of 3.2mm was carried out, and Izod impactive strength with a notch was measured using the Izod impact tester (minimax CS made from custom-made science tee FIKKU- 138TI molds).

[0148]

[Table 1]

表1

		応 用 例	
		1	2 (比較)
配 合 組 成 (重量部)	ポリプロピレン (MA8)	50	50
	ポリ (2, 6-ジメチル-1, 4-フェニレンエーテル)	50	50
	ブロック共重合体 (実施例1)	20	0
評 価 結 果	アイゾット衝撃強度 (kg-cm/cm ²)	6.8	2.1
	曲 げ 弾 性 率 (kg/cm ²)	13,000	13,000

[0149]

[Effect of the Invention] While the thermoplastics which has the shock resistance excellent in itself, and has the outstanding mechanical strength is obtained according to the manufacture approach of this invention, the outstanding compatibilizer of polyphenylene ether, polyolefine or polyolefine, and high impact polystyrene is obtained by the outstanding reforming material list to polyolefine, polystyrene, or polyphenylene ether.

TECHNICAL FIELD

[Industrial Application] This invention relates to the manufacture approach of a block copolymer of combining the aromatic series vinyl compound polymer which has an unsaturated bond at the

chain end, and the olefin system polymer which has an unsaturated bond at the chain end.
[0002] The block copolymer obtained by this is also the outstanding compatibilizer of polyphenylene ether, polyolefine or polyolefine, and high impact polystyrene at the outstanding modifier list to polyolefine, polystyrene, or polyphenylene ether while being thermoplastics which has the shock resistance excellent in itself.

PRIOR ART

[Description of the Prior Art] the homopolymer of an alpha olefin (ethylene shall be included in this invention) or its copolymer is cheap -- in addition, since it has the outstanding mechanical strength, gloss, transparency, a moldability, moisture resistance, and chemical resistance, it is independent or is used widely as a polymer blend component. However, since the molecular structure is a non-polarity, an alpha olefin polymer is lacking in compatibility with others and the matter, and an adhesive property, printing nature, or the compatibility in a polymer blend is remarkably inferior in it.

[0004] In order to improve this, many methods of carrying out the graft polymerization of the monomer in which a radical polymerization is possible to an alpha olefin polymer, and manufacturing a denaturation polymer have been tried for many years.

[0005] However, generally, a radical graft polymerization method has neither a rate of a graft, nor fully high graft efficiency, and since radical polymerization initiators, such as organic or an inorganic peroxide, are used in many cases, it has many problems -- it is easy to produce molecule cutting and crosslinking reaction of a trunk polymer by which graft polymerization should be carried out.

[0006] Various proposals are made for the purpose of solving such a point. For example, suppressing molecule cutting and bridge formation of a trunk polymer in JP,57-98508,A and JP,2-269110,A each official report, and raising the rate of a graft of a monomer to it using the reactivity of the unsaturated bond of the copolymer of an alpha olefin and a nonconjugated diene monomer, is indicated.

[0007] However, this partial saturation copolymer is a nonconjugated diene monomer copolymeric is not necessarily high, and it is further hard to say that the radical graft reaction to this partial saturation copolymer is not necessarily practically completed in viewpoints, such as molecule cutting of the rate of a graft of a monomer, graft efficiency, or a trunk polymer.

[0008] Moreover, chain end double bond HEHAROGEN of the polyolefine obtained by Kaminsky mold Ziegler-Natta catalyst is made to add as approaches other than a radical graft polymerization method, and the method (JP,62-158709,A) of obtaining the block copolymer of an alpha olefin and styrene by the coupling reaction of it and living polystyryl-lithium is learned.

[0009] However, since an unreacted halogen remains in the manufactured copolymer, if this approach carries out melting kneading like extrusion molding or injection molding, coloring and degradation of a copolymer will tend to take place.

[0010] Furthermore, the method (JP,60-20918,A, Eur.Polym.J.17, 1175, 1981, Makromol.Chem.181, 1815, and 1980) of obtaining a block copolymer with polyolefine, polystyrene, or PORUBUTA diene is also learned by the so-called active-spot transformation method of the anionic polymerization active spot and the Ziegler Natta mold polymerization active spot.

[0011] However, these approaches have various troubles, like it is difficult to obtain the decline in the block copolymerization effectiveness by the thing with low (about 10%) active-spot

conversion efficiency, and the controlled copolymer of molecular weight which is made into the purpose.

[0012] Moreover, although the method (JP,5-39331,A) of obtaining a block copolymer from the alpha olefin polymer and anionic polymerization nature monomer which have an unsaturated bond at the chain end is also learned, on the conditions in which anionic polymerization is possible, polyolefine needs to melt into a polymerization solvent and the molecular weight and the stereoregularity of polyolefine which can be used are restricted.

EFFECT OF THE INVENTION

[Effect of the Invention] While the thermoplastics which has the shock resistance excellent in itself, and has the outstanding mechanical strength is obtained according to the manufacture approach of this invention, the outstanding compatibilizer of polyphenylene ether, polyolefine or polyolefine, and high impact polystyrene is obtained by the outstanding reforming material list to polyolefine, polystyrene, or polyphenylene ether.

TECHNICAL PROBLEM

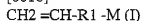
[Problem(s) to be Solved by the Invention] This invention solves the above-mentioned trouble and it aims at offering the manufacture approach of a copolymer of there not being molecule cutting or generating of gelation, and having high copolymerization effectiveness.

MEANS

[Means for Solving the Problem] This invention is the manufacture approach of the block copolymer characterized by combining the silane or Si-H coupling which has two or more Si-H coupling for a following component (a) and a following component (b) using the polyorgano hydrogen siloxane which it has two or more pieces.

[0015] (a) The following general formula (I)

[0016]



[0017] (R1 expresses the hydrocarbon group of carbon numbers 3-20 among a formula, and M expresses an alkali-metal atom)

[0018] The aromatic series vinyl compound polymer which comes out and is obtained using the anionic initiator shown and which has an unsaturated bond at the chain end [0019] (b) The olefin system polymer which has an unsaturated bond at the chain end [0020] Hereafter, this invention is explained to a detail.

[0021] The anionic initiator used by <component (a)> (1) anionic-initiator this invention is a compound shown by the general formula (I).

[0022]



[0023] (R1 expresses the hydrocarbon group of carbon numbers 3-20 among a formula, and M expresses an alkali-metal atom)

[0024] an upper type -- setting -- R1 a carbon number -- desirable -- 3-15 -- it is 3-10 more preferably.

[0025] As an example of M, alkali-metal atoms, such as a lithium, sodium, and a potassium, are

mentioned, among these it is a lithium atom preferably.

[0026] Although not limited, especially the synthetic approach of the above-mentioned anionic initiator (I) can make the compound and alkali metal which are usually shown by the following general formula (II) able to react, and can be acquired.

[0027]

$\text{CH}_2=\text{CH-R1-X (II)}$

[0028] (R1 expresses the hydrocarbon group of carbon numbers 3-20 among a formula, and X expresses a halogen atom)

[0029] As an example of this anionic initiator (I), although 4-pentenyl lithium, 5-HECHISE nil lithium, 7-OKUTE nil lithium, 4-pentenyl sodium, 5-hexenyl sodium, 4-pentenyl potassium, a 5-hexenyl potassium, etc. are mentioned, a desirable thing is 4-pentenyl lithium.

[0030] (2) As an example of an aromatic series vinyl compound aromatic series vinyl compound, for example, styrene, alpha methyl styrene, alpha-methoxy styrene, methyl styrene, dimethyl styrene, 2 and 4, 6-trimethyl styrene, chloro styrene, dichloro styrene, bromostyrene, nitro styrene, chloromethyl styrene, cyano styrene, t-butyl styrene, vinyl naphthalene, etc. are mentioned, and styrene, alpha methyl styrene, and methyl styrene are desirable especially. these are independent -- or two or more sorts can be used together and it can use.

[0031] Moreover, in the range which does not exceed 50-mol %, copolymerization of these aromatic series vinyl compound and the copolymerizable monomer may be carried out, and they may be used. Copolymerization of these monomers may be carried out with which gestalten, such as random or a block. As these examples, they are a butadiene, an isoprene, methacrylic ester, hexamethyl cyclotrisiloxane, etc.

[0032] (3) -100-200 degrees C of -90-150 degrees C of conditions which carry out the polymerization of the aromatic series vinyl compound to a chain end using the manufacture above-mentioned anionic initiator (I) of an aromatic series vinyl compound polymer (a) which has an unsaturated bond can be more preferably performed under ordinary pressure, reduced pressure, or pressurization at the temperature of -80-100 degrees C.

[0033] as a solvent which can be used in the above-mentioned polymerization, aprotic polar-solvents [, such as aromatic hydrocarbon; TERATO hydronalium furans, such as alicyclic hydrocarbon; benzene such as aliphatic hydrocarbon; cyclohexanes, such as n-hexane and n-heptane and decahydronaphthalene, toluene, o-, m-, or para xylene, dioxane, ethyl ether, a pyridine and a jig rim,]; etc. can be used, for example. These solvents may be independent or mixture is sufficient as them.

[0034] the number average molecular weight (henceforth "Mn") generally according to gel-permeation-chromatography (henceforth "GPC") measurement although the molecular weight of the aromatic series vinyl compound polymer (a) which has an unsaturated bond at this chain end is arbitrary -- 500-1,000,000 -- desirable -- 500-500,000 -- it is 1,000-100,000 more preferably.

[0035] The olefin system polymers which have an unsaturated bond at the chain end of the component (b) used by <component (b)> (1) alpha-olefin this invention are carbon numbers 2-12 and a copolymer which makes a principal component preferably the homopolymer of the alpha olefin of 2-8, or them. As an example of these alpha olefins, ethylene, a propylene, 1-butene, 1-hexene, a 3-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, 3, and 3-dimethyl-1-butene, 4, and 4-dimethyl-1-pentene, A 3-methyl-1-hexene, 4-methyl-1-hexene, 4, and 4-dimethyl-1-hexene, A 5-methyl-1-hexene, an allyl compound cyclopentane, an allyl compound cyclohexane, allyl compound benzene, a 3-cyclohexyl-1-butene, a vinyl cyclopropane, a vinyl cyclohexane, a 2-vinyl bicyclo [2.2.1]-heptane, etc. can be mentioned. As an example desirable [

among these], ethylene, a propylene, 1-butene, 1-hexene, a 3-methyl-1-butene, 3-methyl-1-pentene, 4-methyl-1-pentene, a 3-methyl-1-hexene, etc. can be mentioned, and ethylene, a propylene, 1-butene, 1-hexene, a 3-methyl-1-butene, or 4-methyl-1-pentene is especially desirable. The number of these alpha olefins one, and even if it uses two or more kinds, they do not interfere. When using two or more sorts of alpha olefins, these alpha olefins may be distributed at random in a partial saturation polymer, or it may be distributed in block.

[0036] (2) The olefin system polymer (b) which has an unsaturated bond at the chain end used for a chain end by manufacture this invention of the olefin system polymer (b) which has an unsaturated bond can be manufactured by two sorts of following approaches.

[0037] ** The approach of carrying out copolymerization of the above-mentioned alpha olefin, and alpha and omega-diene using a Ziegler-Natta catalyst. in this case -- although 1, 9-deca diene, 1, 13-tetra-deca diene, a divinylbenzene, etc. are mentioned and especially a limit does not have the amount of copolymerization of such dienes as an example of alpha to be used and omega-diene -- 0.01-30-mol % -- it is 0.05-20-mol % preferably. Less than [0.01 mol %], a block-copolymer yield becomes low at joint reaction time with a component (a), and if 30-mol % is exceeded, it will be easy to generate gelation etc. at the time of alpha olefin, alpha, and omega-diene copolymerization. Even if these alpha and omega-diene use two or more kinds even when they are independent or, they do not interfere.

[0038] ** The approach of carrying out the polymerization of the above-mentioned alpha olefin using the catalyst which consists of the following component (i) and (ii).

(i) A component (i) is a periodic table IVB-VIB group transition-metals compound which has at least one conjugated five-membered ring ligand. Specifically, it is shown by the following general formula (III) or the general formula (IV).

[0039]

Qa [C5 H5-a-b(R2) b] and [C5 H5-a-c(R3) c] MeXY (III) [0040]

Sa [C5 H5-a-d(R4) d] ZMeXY (IV)

[0041] Here, Q expresses the affinity radical which constructs a bridge in two conjugated five-membered ring ligands, and S expresses a conjugated five-membered ring ligand and the affinity radical which constructs a bridge in Z sets. Specifically, it is [0042]. (b) Low-grade alkylene, its low-grade alkyl, or a phenyl permutation derivative, Preferably Methylene, ethylene, an isopropenyl pyrene, phenylmethyl methylene, (b) silylenes, such as diphenylmethylene and cyclohexylene, thru/or oligo silylene, or the low-grade alkyl or a phenyl permutation derivative -- desirable -- silylene -- Dimethylsilylene, phenylmethyl silylene, diphenyl silylene, Germanium (Ha), such as disilylene and tetramethyl disilylene, Lynn, On the hydrocarbon-group [concrete target (CH3) containing nitrogen, boron, or aluminum, 2 germanium, (C six H5) 2germanium, P (CH3), P (C six H5), N (C four H9), N (C six H5), B (CH3), B (C four H9), B (C six H5), aluminum (C six H5), aluminum (CH3 O), etc. are] etc. In these, they are an alkylene group or a silylene radical preferably. a is 0 or 1.

[0043] Also although the conjugated five-membered ring ligand expressed with [C5 H5-a-b(R2) b], [C5 H5-a-c(R3) c], or [C5 H5-a-d(R4) d] is separately defined in the above-mentioned general formula, respectively It is R2 and R3 to b, c and d, and a list. And R4 Since the definition itself is the same (detail postscript), it cannot be overemphasized that you may differ even if these three conjugated five-membered ring radicals are the same.

[0044] One example of this conjugated five-membered ring radical is the cyclopentadienyl group (there are no substituents other than the bridge formation radicals Q and S) of b=0 (c=0 or d=0). Although one example of R2 (R3 or R4) is a hydrocarbon group (C1 - C20, preferably C1 -

C12) when this conjugated five-membered ring radical is $b \neq 0$ ($c \neq 0$ or $d \neq 0$) and is what has a substituent. Even if it has combined this hydrocarbon group with the cyclopentadienyl group as a univalent radical. Moreover, when two or more of these exist, the two pieces may join mutually together by each other end, and may form the condensed ring of a ring, i.e., a cyclopentadiene ring, with a part of cyclopentadienyl group concerned. That in which R2 (R3 or R4) shares the double bond of the cyclopentadienyl group concerned, and the latter example of representation forms the condensation six membered ring, i.e., this conjugated five-membered ring radical, is an indenyl group or a fluorenyl group. That is, the example of representation of this conjugated five-membered ring radical is a permutation or an unsubstituted cyclopentadienyl group, an indenyl group, or a fluorenyl group.

[0045] R2 and R3 And R4 C1 of the above respectively - C20 -- desirable -- the outside of the hydrocarbon group of C1 - C12 -- a halogen atom -- [-- for example fluorine, chlorine, and bromine], an alkoxy group (for example, thing of C1 - C12), and a silicon content hydrocarbon group -- [-- for example silicon -- an atom - Si -- ((- R --) (R') (R'')) -- a form -- containing -- a carbon number -- one - 24 -- about -- a radical --] -- Lynn -- content -- a hydrocarbon group -- [-- for example Lynn -- an atom - P -- ((- R --) -- ((- R -- ' --) -- a form -- containing -- a carbon number -- one - 18 -- about -- a radical --] -- nitrogen -- content -- a hydrocarbon group -- [-- for example nitrogen -- an atom - N -- ((- R --) -- ((- R -- ' --) -- a form -- containing -- a carbon number -- one - 18 -- about -- a radical --] -- or -- boron -- content -- a hydrocarbon group -- [-- for example, -- boron -- an atom - B -- ((- R --) -- ((- R -- ' --) -- a form -- containing -- a carbon number -- one - 18 -- about -- a radical --] -- it is . b (c or d) is two or more, and when two or more R2 (R3 or R4) exists, even if they are the same, they may differ.

[0046] b, c, and d express the integer with which are satisfied of $0 < b \leq 4$, $0 < c \leq 4$, and $0 < d \leq 4$, when a is 0 and a is 1 about $0 < b \leq 5$, $0 < c \leq 5$, and $0 < d \leq 5$.

[0047] Me -- periodic-table IVB-VIB group transition metals -- they are titanium, a zirconium, or a hafnium preferably. It is a zirconium especially preferably.

[0048] Z -- oxygen (-O-), sulfur (-S-), and carbon numbers 1-20 -- desirable -- the alkoxy group of 1-10, and carbon numbers 1-20 -- desirable -- the thio alkoxy group of 1-12, and carbon numbers 1-40 -- desirable -- the silicon content hydrocarbon group of 1-18, and carbon numbers 1-40 -- desirable -- the nitrogen content hydrocarbon group of 1-18, and carbon numbers 1-40 -- it is the Lynn content hydrocarbon group of 1-18 preferably. A part of Z sets have combined with S sets which are affinity radicals at the time of $a = 1$.

[0049] X and Y -- the each hydrogen atom; halogen atom; carbon numbers 1-20 -- desirable -- the hydrocarbon-group; carbon numbers 1-20 of 1-10 -- desirable -- the alkoxy group; amino-group; carbon numbers 1-20 of 1-10 -- desirable -- Lynn content hydrocarbon-group [of 1-12] (specifically for example, diphenylphosphine radical);, or carbon numbers 1-20 -- desirable -- the silicon content hydrocarbon group of 1-12 -- [-- specifically, it is trimethylsilyl radical and bis(trimethylsilyl) methyl group]. Even if X and Y are the same, they may differ. A halogen atom and a hydrocarbon group are [among these] desirable.

[0050] The example of this transition-metals compound in case Me is a zirconium is as follows.

[0051] (b) The transition metals which do not have the joint radical which constructs a bridge but have two conjugated five-membered ring ligands, for example, [0052]

Bis(cyclopentadienyl)zirconiumdichloride, bis(methylcyclopentadienyl)zirconiumdichloride, bis(dimethylcyclopentadienyl)zirconiumdichloride, bis(trimethylcyclopentadienyl)zirconiumdichloride, bis(tetramethylcyclopentadienyl) zirconium dichloride, [0053] Bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(n-

butylcyclopentadienyl) zirconium dichloride, bis(indenyl)zirconiumdichloride, bis(fluorenyl) zirconium dichloride, a bis(cyclopentadienyl) zirconium monochrome RIDOMONO hydride, [0054] Bis(cyclopentadienyl) methyl zirconium mono-chloride, bis(cyclopentadienyl) ethyl zirconium mono-chloride, bis(cyclopentadienyl) phenyl zirconium mono-chloride, bis(cyclopentadienyl) zirconium dimethyl, bis(cyclopentadienyl) zirconium diphenyl, [0055] Bis(cyclopentadienyl)zirconiumdineopentyl, bis(cyclopentadienyl) zirconium JIHAIDORAIDO, zirconium dichloride (indenyl (cyclopentadienyl)), zirconium dichloride (fluorenyl (cyclopentadienyl)), etc.

[0056] (b) The transition-metals compound which has two five-membered ring ligands which constructed the bridge by the alkylene group, for example, [0057] Methylenebis (indenyl) zirconium dichloride, ethylene bis(indenyl)zirconiumdichloride, ethylene bis(indenyl) zirconium mono-hydride monochloride, ethylene bis(indenyl) methyl zirconium mono-chloride, ethylene bis(indenyl) zirconium mono-methoxide MONOKURORIDO, [0058] Ethylene bis(indenyl) zirconium JIETOKISHIDO, ethylene bis(indenyl) zirconium dimethyl, ethylene bis(4, 5, 6, 7-tetrahydroindenyl) zirconium dichloride, ethylene bis(2-methyl indenyl) zirconium dichloride, ethylene bis(2-ethyl indenyl) zirconium dichloride, [0059] Ethylene bis(2, 4-dimethyl indenyl) zirconium dichloride, Ethylene (2, 4-dimethylcyclopentadienyl) (3', 5'-dimethylcyclopentadienyl) zirconium dichloride, Ethylene (2-methyl-4-tert-butylcyclopentadienyl) (3'-tert-butyl-5'-methylcyclopentadienyl) zirconium dichloride, Ethylene (2, 3, 5-trimethylcyclopentadienyl) (2', 4', 5'-trimethylcyclopentadienyl) zirconium dichloride, isopropylidene bis(indenyl)zirconiumdichloride, [0060] Isopropylidene (2, 4-dimethylcyclopentadienyl) (3', 5'-dimethylcyclopentadienyl) zirconium dichloride, Isopropylidene (2-methyl-4-tert-butylcyclopentadienyl) (3'-tert-butyl-5'-methylcyclopentadienyl) zirconium dichloride, Methylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium dichloride, Methylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium chloride hydride, methylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium dimethyl, [0061] Methylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium diphenyl, Methylene (cyclopentadienyl) (trimethylcyclopentadienyl) zirconium dichloride, Methylene (cyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride, Isopropylidene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium dichloride, isopropylidene (cyclopentadienyl) (2, 3, 4, 5-tetramethylcyclopentadienyl) zirconium dichloride, [0062] Isopropylidene (cyclopentadienyl) (3-methyl indenyl) zirconium dichloride, isopropylidene (cyclopentadienyl) (fluorenyl) zirconium dichloride, isopropylidene (2-methylcyclopentadienyl) (fluorenyl) zirconium dichloride, isopropylidene (2, 5-dimethylcyclopentadienyl) (3', 4'-dimethylcyclopentadienyl) zirconium dichloride, isopropylidene (2, 5-dimethylcyclopentadienyl) (fluorenyl) zirconium dichloride, [0063] Ethylene (cyclopentadienyl) (3, 5-dimethylcyclopentadienyl) zirconium dichloride, Ethylene (cyclopentadienyl) (fluorenyl) zirconium dichloride, Ethylene (2, 5-dimethylcyclopentadienyl) (fluorenyl) zirconium dichloride, Ethylene (2, 5-diethyl cyclopentadienyl) (fluorenyl) zirconium dichloride, Diphenylmethylene (cyclopentadienyl) (3, 4-diethyl cyclopentadienyl) zirconium dichloride, Cyclohexylidene (cyclopentadienyl) (fluorenyl) zirconium dichloride, cyclohexylidene (2, 5-dimethylcyclopentadienyl) (3', 4'-dimethylcyclopentadienyl) zirconium dichloride, etc.

[0064] (c) The transition-metals compound which has a silylene radical bridge formation five-membered ring ligand, for example, [0065] Dimethylsilylene bis(indenyl)zirconiumdichloride, dimethylsilylene bis(4, 5, 6, 7-tetrahydroindenyl) zirconium dichloride, dimethylsilylene bis(2-methyl indenyl) zirconium dichloride, dimethylsilylene bis(2, 4-dimethyl indenyl) zirconium

dichloride, dimethylsilylene bis(2-methyl - 4, 5, 6, 7-tetrahydroindenyl) zirconium dichloride, [0066] Dimethylsilylene (2, 4-dimethylcyclopentadienyl) (3', 5'-dimethylcyclopentadienyl) zirconium dichloride, Phenylmethyl silylene bis(indenyl)zirconiumdichloride, Phenylmethyl silylene bis(4, 5, 6, 7-tetrahydroindenyl) zirconium dichloride, Phenylmethyl silylene (2, 4-dimethylcyclopentadienyl) (3', 5'-dimethylcyclopentadienyl) zirconium dichloride, Phenylmethyl silylene (2, 3, 5-trimethylcyclopentadienyl) (2', 4', 5'-trimethylcyclopentadienyl) zirconium dichloride, [0067] Phenylmethyl silylene bis(tetramethylcyclopentadienyl) zirconium dichloride, diphenyl silylene bis(indenyl)zirconiumdichloride, tetramethyl disilylene bis(indenyl)zirconiumdichloride, tetramethyl disilylene bis(cyclopentadienyl)zirconiumdichloride, tetramethyl disilylene (3-methylcyclopentadienyl) (indenyl) zirconium dichloride, [0068] Dimethylsilylene (cyclopentadienyl) (3, 4-dimethylcyclopentadienyl) zirconium dichloride, Dimethylsilylene (cyclopentadienyl) (trimethylcyclopentadienyl) zirconium dichloride, Dimethylsilylene (cyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride, Dimethylsilylene (cyclopentadienyl) (3, 4-diethyl cyclopentadienyl) zirconium dichloride, dimethylsilylene (cyclopentadienyl) (triethyl cyclopentadienyl) zirconium dichloride, [0069] Dimethylsilylene (cyclopentadienyl) (tetraethyl cyclopentadienyl) zirconium dichloride, dimethylsilylene (cyclopentadienyl) (fluorenyl) zirconium dichloride, dimethylsilylene (cyclopentadienyl) (2, 7-G t-butyl fluorenyl) zirconium dichloride, dimethylsilylene (cyclopentadienyl) (octahydro fluorenyl) zirconium dichloride, dimethylsilylene (2-methylcyclopentadienyl) (fluorenyl) zirconium dichloride, [0070] Dimethylsilylene (2, 5-dimethylcyclopentadienyl) (fluorenyl) zirconium dichloride, Dimethylsilylene (2-ethylcyclopentadienyl) (fluorenyl) zirconium dichloride, Dimethylsilylene (2, 5-diethyl cyclopentadienyl) (fluorenyl) zirconium dichloride, Diethylsilylene (2-methylcyclopentadienyl) (2', 7'-G t-butyl fluorenyl) zirconium dichloride, Dimethylsilylene (2, 5-dimethylcyclopentadienyl) (2', 7'-G t-butyl fluorenyl) zirconium dichloride, [0071] Dimethylsilylene (2-ethylcyclopentadienyl) (2', 7'-G t-butyl fluorenyl) zirconium dichloride, Dimethylsilylene (diethyl cyclopentadienyl) (2', 7'-G t-butyl fluorenyl) zirconium dichloride, Dimethylsilylene (methylcyclopentadienyl) (octahydro fluorenyl) zirconium dichloride, Dimethylsilylene (dimethylcyclopentadienyl) (octahydro fluorenyl) zirconium dichloride, Dimethylsilylene (ethylcyclopentadienyl) (octahydro fluorenyl) zirconium dichloride, dimethylsilylene (diethyl cyclopentadienyl) (octahydro fluorenyl) zirconium dichloride, etc. [0072] (d) The transition-metals compound which has the five-membered ring ligand over which the bridge was constructed by the hydrocarbon group containing germanium, aluminum, boron, Lynn, or nitrogen, for example, [0073] Dimethyl germanium bis(indenyl)zirconiumdichloride, dimethyl germanium (cyclopentadienyl) (fluorenyl) zirconium dichloride, methyl aluminum bis(indenyl)zirconiumdichloride, phenyl aluminum bis(indenyl)zirconiumdichloride, phenyl phosphino bis(indenyl)zirconiumdichloride, [0074] ECHIRUHO llano bis(indenyl)zirconiumdichloride, phenylamino bis(indenyl)zirconiumdichloride, phenylamino (cyclopentadienyl) (fluorenyl) zirconium dichloride, etc. are illustrated. [0075] (e) The transition-metals compound which has one five-membered ring ligand, for example, [0076] Pentamethylcyclopentadienyl bis(phenyl) amide zirconium dichloride, indenyl bis(phenyl) amide zirconium dichloride, pentamethylcyclopentadienyl bis(trimethylsilyl) amide zirconium dichloride, pentamethylcyclopentadienyl phenoxy JIRUNIMUMU dichloride, dimethylsilylene (tetramethylcyclopentadienyl) phenyl amide zirconium dichloride, [0077] Dimethylsilylene (tetramethylcyclopentadienyl)-tert-butyl amide zirconium dichloride, dimethylsilylene (indenyl) cyclohexyl amide zirconium dichloride, dimethylsilylene

(tetrahydroindenyl) DESHIRU amide zirconium dichloride, dimethylsilylene (tetrahydroindenyl) (trimethylsilyl) amide zirconium dichloride, dimethyl germane (tetramethylcyclopentadienyl) (phenyl) amide zirconium dichloride, etc. are illustrated.

[0078] (**) Moreover, what transposed the chlorine of the compound of the above-mentioned (b) - (e) to a bromine, iodine, a hydride, methyl, phenyl, etc. is usable.

[0079] Furthermore, in this invention, the compound which changed the central metal of the zirconium compound illustrated to the above-mentioned (b) - (**) as a component (i) from the zirconium to titanium, a hafnium, niobium, molybdenum, or a tungsten can also be used.

[0080] A zirconium compound, a hafnium compound, or a titanium compound is [among these] desirable. The titanium compound, zirconium compound, or hafnium compound which constructed the bridge by the alkylene group or the silylene radical is more desirable.

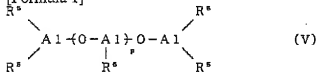
[0081] (ii) -- a component (ii) -- (**) -- an aluminum oxy compound and (**) -- they are Lewis acid or (Ha) the ionicity compound which it reacts with a component (i) and can change a component (i) into a cation.

[0082] The thing with Lewis acid can also be regarded as "an ionicity compound which it reacts with a component (i) and can change a component (i) into a cation." Therefore, suppose that the compound belonging to both "Lewis acid" and "ionicity compound which it reacts with a component (i) and can change a component (i) into a cation" is understood as the thing belonging to either.

[0083] As an aluminum oxy compound, there is specifically a general formula (V), (following VI), or (VII) the following compound shown.

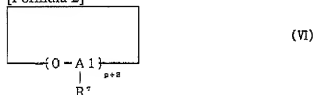
[0084]

[Formula 1]



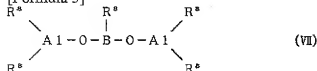
[0085]

[Formula 2]



[0086]

[Formula 3]



[0087] (the inside of a formula, and p -- 0-40 -- desirable -- the integer of 2-30 -- it is -- R5, R6, and R7 and R8 -- an each hydrogen atom -- or -- desirable -- carbon numbers 1-10 -- the hydrocarbon group of carbon numbers 1-6 is expressed more preferably)

[0088] The compound of a general formula (V) and (VI) is a compound called alumoxane, and is

a product obtained by the reaction of one kind of trialkylaluminum or two or more kinds of trialkylaluminums, and water. Specifically, the trialkylaluminum of one kind of (b), the methylalumoxane obtained from water, ethylalumoxane, propyl alumoxane, buthylalumoxane, isobuthylalumoxane, the trialkylaluminum of two kinds of (b)s and the methylethyl alumoxane obtained from water, methylbutyl alumoxane, methyl isobuthylalumoxane, etc. are illustrated. In these, especially a desirable thing is methyl ARUMOKISA or methyl isobuthylalumoxane.

[0089] These alumoxane can also be used [also using two or more sorts together by the inside of each group, and each between groups one, or] together with other alkylaluminum compounds, such as trimethylaluminum, triethylaluminum, triisobutylaluminum, and dimethyl aluminum chloride, possible.

[0090] These alumoxane can be prepared by well-known various approaches, and the following approaches are specifically illustrated.

[0091] (b) the approach to which trialkylaluminum makes react with direct water using suitable organic solvents, such as toluene, benzene, and the ether, and (**) -- the approach of mixing the approach and the (d) trimethylaluminum to which the hydrate of the salt hydrate which has trialkylaluminum and water of crystallization, for example, a copper sulfate, and an aluminum sulfate, the approach and the trialkylaluminum (Ha) made to react, and the moisture into which silica gel etc. be infiltrated be made to react, and triisobutylaluminum, and making it react with direct water using suitable organic solvents, such as toluene, benzene, and the ether, and [0092] (e) Mix trimethylaluminum and triisobutylaluminum. How to carry out a pyrogenetic reaction to hydrates, such as the salt hydrate which has water of crystallization, for example, a copper sulfate, and an aluminum sulfate, After infiltrating moisture into (**) silica gel etc. and processing by triisobutylaluminum, The approach, (g) methylalumoxane, and isobuthylalumoxane which carry out additional processing by trimethylaluminum are compounded by the well-known approach. How to put the salt which has water of crystallization, such as copper-sulfate 5 monohydrate, into aromatic hydrocarbon solvents, such as the approach of carrying out specified quantity mixing of these 2 component, and carrying out a pyrogenetic reaction, (h) benzene, and toluene, and make it react with the about -40-40-degree C bottom trimethylaluminum of a temperature condition. In this case, the amounts of the water to be used are usually 0.5-1.5 in a mole ratio to trimethylaluminum. Thus, the obtained methylalumoxane is the polymer of linear or annular organic aluminum.

[0093] The compound shown by the general formula (VII) is one kind of trialkylaluminum or two or more kinds of trialkylaluminums, and the following general formula (VIII).

[0094]

$R_9-B(OH)_2$ (VIII)

[0095] it can come out and can obtain by the reaction of the mole ratios 10:1-1:1 with the alkyl boron acid (the inside of a formula, and R_9 -- carbon numbers 1-10 -- the ARUKI radical of carbon numbers 1-6 is expressed preferably) shown. concrete -- (**) -- trimethylaluminum, the reactant of 2:1 of a methyl boron acid, and (**) -- triisobutylaluminum, the reactant of 2:1 of a methyl boron acid and trimethylaluminum (Ha), triisobutylaluminum, the reactant of 1:1:1 of a methyl boron acid and (d) trimethylaluminum, the reactant of 2:1 of an ethyl boron acid, (e) triethylaluminum, the reactant of 2:1 of a butyl boron acid, etc. are illustrated. The compound of these general formulas (VII) is possible also for using two or more sorts, and can also be used together with other alkylaluminum compounds, such as alumoxane shown by the general formula (V) or (VI), and trimethylaluminum, triethylaluminum, triisobutylaluminum, dimethyl aluminum chloride.

[0096] Moreover, as an ionicity compound which it reacts with a component (i) and can change a component (i) into a cation, there are some which are shown by the general formula (IX).

[0097]

[K] e+[Z] e- (IX)

[0098] Here, K is the cation component of ionicity, for example, a carbonium cation, a tropylium cation, an ARUMONIUM cation, an oxonium cation, a sulfonium cation, a HOSUFONIUM cation, etc. are mentioned. Moreover, a metaled cation, a cation of an organic metal, etc. which itself is easy to be returned are mentioned. As an example of these cations, the (b) triphenyl carbonium, The diphenyl carbonium, cyclo hepta-TORIENIUM, indie NIUM, Triethyl ammonium, TORIPURO pill ammonium, tributyl ammonium, N and N-dimethyl anilinium, dipropyl ammonium, dicyclohexyl ammonium, Triphenyl phosphonium, trimethyl phosphonium, the Tori (dimethylphenyl) phosphonium, There are the Tori (methylphenyl) phosphonium, triphenylsulfonium, triphenyl oxonium, triethyl oxonium, kinky thread RIUMU and complex ion, golden ion, platinum ion, a copper ion, palladium ion, mercury ion, ferro SENTUMU ion, etc.

[0099] Z in the above-mentioned general formula (IX) is the anion component of ionicity, and it is the component (generally non-coordination) which serves as an opposite anion to the cation kind from which the component (i) was changed, for example, an organic boron compound anion, an organoaluminium compound anion, an organic gallium compound anion, an organic phosphorous compound anion, an organic arsenical compound anion, an organic-antimony-compounds anion, etc. are mentioned. concrete -- (**) -- tetra-phenyl boron and tetrakis (3, 4, 5-trifluoro phenyl) boron -- Tetrakis (3, 5-JI (trifluoromethyl) phenyl) boron, Tetrakis (3, 5-JI (t-butyl) phenyl) boron, tetrakis (pentafluorophenyl) boron, (**) -- tetra-phenyl aluminum and tetrakis (3, 4, 5-trifluoro phenyl) aluminum -- Tetrakis [3 and 5-JI (trifluoromethyl) phenyl] aluminum, Tetrakis [3 and 5-JI (t-butyl) phenyl] aluminum, tetrakis (pentafluorophenyl) aluminum, A tetra-phenyl gallium, a tetrakis (3, 4, 5-trifluoro phenyl) gallium, (Ha) A tetrakis [3 and 5-JI (trifluoromethyl) phenyl] gallium, A tetrakis [3 and 5-JI (t-butyl) phenyl] gallium, a tetrakis (pentafluorophenyl) gallium, (**) -- tetra-phenyl phosphorus and tetrakis (pentafluorophenyl) Lynn -- (**) -- tetra-FENIRUHI -- base and a tetrakis (pentafluorophenyl) arsenic -- (**) -- tetra-phenyl antimony, tetrakis (pentafluorophenyl) antimony, (g) deca borate, undeca borate, KARUBA dodeca borate, deca chloro deca borate, etc. are illustrated.

[0100] Moreover, if Lewis acid, especially a component (i) are used as Lewis acid convertible into a cation, various organic boron compounds, a metal halogenated compound, or solid acid is illustrated. concrete -- (**) -- triphenyl boron and tris (3, 5-difluoro phenyl) boron -- Organic boron compounds, such as tris (pentafluorophenyl) boron; A (b) aluminum chloride, The aluminium bromide, an aluminium iodide, a magnesium chloride, a magnesium bromide, Magnesium iodide, bromine chloride magnesium, chlorination magnesium iodide, bromination -- magnesium iodide, a magnesium chloride hydride, and magnesium chloride hydronalium oxide -- magnesium bromide hydronalium oxide, chlorination magnesium alkoxide, and bromination -- solid acid, such as metal halogenated compound [, such as magnesium alkoxide,]; or (Ha) a silica alumina, and an alumina, etc. is mentioned.

[0101] these ionicity compounds and Lewis acid -- as a component (ii) -- independent -- it can also use -- a general formula (V) and (VI) -- or (VII) can be used together with an aluminum oxy compound. Moreover, it is also possible to use together with organoaluminium compounds, such as trimethylaluminum, triethylaluminum, triisobutylaluminum, a diethyl aluminum phenoxide, and dimethyl aluminum chloride, as trialkylaluminium and dialkyl aluminum mono-halide,

monoalkyl aluminum dihalide and alkylaluminum sesquihalide, the things that a part of these alkyl groups replaced with the list with the phenoxy group, and these examples.

[0102] (iii) The desirable catalyst of this invention can be acquired by making the bottom of existence of the monomer to which it is in a polymerization tank or the polymerization of an above-mentioned component (i) and an above-mentioned component (ii) should be carried out out of a polymerization tank, or nonexistence contact.

[0103] The amount of the component (i) used by this invention and the component (ii) used is arbitrary. For example, in the case of a solvent polymerization, the amount of the component (i) used is 10⁻⁷-10² as a transition-metals atom. Within the limits of millimol/liter, and 10⁻⁴ - 1 millimol / liter is more desirable. In the case of an aluminum oxy compound, as for the mole ratio of aluminum/transition metals, 10-100,000, and 100-20,000 are usually desirable, and its range of 100-10,000 is more desirable. the case where an ionicity compound or Lewis acid is used as a component (ii) on the other hand -- the mole ratio of opposite transition metals -- 0.1-1,000 -- desirable -- 0.5-100 -- it is more preferably used in 1-50.

[0104] Although it is as having described above that the catalyst of this invention is what may contain other components in addition to a component (i) and (ii) As the third component (arbitration component) which can be added to a component (i) and (ii) For example, active hydrogen content compounds, such as H₂ O, a methanol, ethanol, and a butanol; The ether, Electron-donative compounds, such as ester and an amine; alkoxy content compounds, such as boric-acid phenyl, dimethyl methoxy aluminum, phosphorous acid phenyl, a tetra-ethoxy silane, and diphenyldimethoxysilane, etc. are mentioned.

[0105] The manufacture approach of the block copolymer in <manufacture of block copolymer> this invention is combining a component (a) and a component (b) by hydrosilylation, and should just have Si-H association in [two or more] 1 molecule as the silane used for hydrosilylation, or a polyorgano hydrogen siloxane.

[0106] As an example of such a silane or a polyorgano hide JIEN siloxane, diethylsilane, phenylsilane, a methylphenyl silane, poly methylhydrogensiloxane, a polyphenyl hydrogen siloxane, etc. are mentioned.

[0107] A reaction condition is -50-200 degrees C in temperature, and can be made to react under ordinary pressure, reduced pressure, or pressurization preferably -100-300 degrees C.

[0108] As a reaction solvent, although an aliphatic hydrocarbon solvent, an alicyclic hydrocarbon solvent, an aromatic hydrocarbon solvent, an aprotic polar solvent, etc. can be used, for example, what may dissolve a component (a) and (b) with both reaction temperature is desirable.

[0109] Moreover, the catalyst for promoting a reaction as occasion demands may be used. As a catalyst, transition-metals compounds, such as Pt, Rh, Pd, and nickel, are usually used. Chloroplatinic acid (H₂ PtCl₂) etc. is mentioned as these examples.

[0110] Reaction time can be set as arbitration by various reaction conditions.

[0111] When the usual application offers the block copolymer obtained by this invention, in this copolymer, an unreacted component (a) and an unreacted component (b) may be included.

EXAMPLE

[Example] Although an example is given to below and this invention is concretely explained to it, this invention is not limited to these.

[0113] The following manufactures were performed under the manufacture high vacuum of an

example of reference 1:4-pentenyl lithium using the breaking seal method. Namely, metal lithium 5g And 5-BUOMO-1-pentene 6g It was made to react for three days at a room temperature in addition to n-heptane 120ml. Next, diethylether 40ml was added to this reaction mixture, the churning back fault was carried out at 0 degree C for 24 hours, and the solvent of the filtrate was distilled off. It was checked that the peak of a vinyl group and the methyl anion origin was observed, and 4-pentenyl lithium had been obtained by 1 H-NMR analysis. Yield was 70%.

[0114] The example 2 of reference: It carried out to the end under the high vacuum using the breaking seal method like the example 1 of synthetic reference of the polystyrene which has an unsaturated bond. Namely, 4-pentenyl lithium 0.08g obtained in the example 1 of reference It dilutes with n-heptane 9.3ml and is styrene 6.2g about this. After being dropped at the bottom of churning in the solution which mixed benzene 200ml and carrying out a polymerization at a room temperature for 2 hours, methanol 2ml was added and the polymerization was stopped. It is methanol 1L about this reaction mixture. It flowed into inside and the polymer which precipitated was dried the ** exception. the obtained polymer (henceforth "Resin A") -- 6.2g it is -- as a result of GPC measurement, Mn was 6,270 and weight average molecular weight (henceforth "Mw") was 8,080. It was checked from the ratio of the peak intensity which originates in the peak intensity originating in the polystyrene principal chain of Resin A, and an end vinyl group by 1 H-NMR analysis that the vinyl group is introduced into all the piece ends of a polymer.

[0115] The example 3 of reference: Set for the example 2 of synthetic reference of the polystyrene which has an unsaturated bond at the end, and it is 7.0g about the amount of 0.04g and styrene in the amount of 4-pentenyl lithium. It carried out like the example 2 of reference except having changed. the obtained polymer (henceforth "Resin B") -- 6.9g it is -- as a result of measurement of GPC, Mn was 14,400 and Mw was 15,600. That the vinyl group is altogether introduced also into the end of Resin B I understand from analysis of 1 H-NMR.

[0116] example of reference 4: -- manufacture of synthetic (1) ethylene bis(indenyl)zirconiumdichloride of the polypropylene which has an unsaturated bond at the end - 300ml glass flask which fully carried out the nitrogen purge -- bis(indenyl) ethane 5.16g And tetrahydrofuran 150ml was inserted in and it cooled to -78 degrees C. Butyl lithium (product made from Aldrich) 25ml (concentration of 1.6 mols/l.) is bet on this for 1 hour, and is dropped at it, and the temperature up was carried out gradually and it was made to flow back after that to reflux temperature for 2 hours.

[0117] On the other hand, a tetrahydrofuran is cooled to -78 degrees C after 100ml insertion in 200ml glass flask which fully carried out the nitrogen purge, and it is 4.7g of zirconium tetrachlorides to it. In addition, the temperature up was gradually carried out to the room temperature. Package addition of this zirconium tetrachloride solution was carried out at 0 degree C into the lithium salt solution of the above-mentioned bis(indenyl) zirconium, the temperature up was carried out to reflux temperature after that, and the reaction was continued at reflux temperature for 16 hours. The generated yellow solid-state was carried out the ** exception, the methanol washed, and it dried under reduced pressure. 1.9g Ethylene bis(indenyl)zirconiumdichloride was obtained.

[0118] (2) manufacture trimethylaluminum 48.2g of methylalumoxane 565ml of included toluene solutions -- the bottom of churning, and 50g of copper-sulfate 5 monohydrates 0 degree C -- 5g every -- it supplied at intervals of 5 minute. Carry out a temperature up to 25 degrees C slowly, and it is made to react at 25 degrees C for 2 hours, and the temperature up of the solution

was carried out to 35 more degrees C, and it was made to react for two days after termination. The solid-state of the copper sulfate which remains was separated and the toluene solution of alumoxane was obtained. The concentration of methylalumoxane was 27.3mg (2.7w/v %)/ml. [0119] (3) Content volume 1.0L equipped with the polymerization agitator and the temperature controller Toluene 400ml fully dehydrated and deoxygenized, methylalumoxane 580mg, and ethylene bis(indenyl)zirconiumdichloride 0.418mg (0.001mmol) were introduced into the autoclave made from stainless steel, and the polymerization was carried out to it at propylene pressure 7kg/cm²G and 40 degrees C for 4 hours. It is 3L after polymerization termination and about a polymerization solution. It is 180g, when it extracts in a methanol, and the polymer was carried out the ** exception and dried. Resin (henceforth "Resin C") was collected. This thing was Mn18,700 and molecular weight distribution (Mw/Mn) 1.99 as a result of GPC measurement.

[0120] The [mm] molar fraction of TORIADDO was 0.888 as a result of 13 C-NMR (JEOL Co., Ltd. make, trade name:JEOL.FX-200) analysis, and all single-sided ends were vinylidene association (0.79 per 1,000 carbon atom).

[0121] The example 5 of reference: Except having changed polymerization temperature to 20 degrees C in the example 4 of synthetic reference of the polypropylene which has a partial saturation radical at the end, carry out like the example 4 of reference and it is 43g. Resin (henceforth "Resin D") was obtained. Mn of this thing was 32,500 and Mw/Mn was 1.93.

[0122] example of reference 6: -- manufacture of synthetic (1) solid-state catalyst component (i) of a propylene and the copolymer of 1 and 9-deca diene -- n-heptane 200ml dehydrated and deoxygenized in the flask which fully carried out the nitrogen purge -- introducing -- subsequently - MgCl₂ 0.4 mols and Ti (O-nC four H₉)₄ 0.8 mols were introduced and it was made to react at 95 degrees C for 2 hours. Temperature was lowered to 40 degrees C after reaction termination, subsequently methyl hydronalium polysiloxane (thing of 20cS) 48ml was introduced, and it was made to react for 3 hours. The generated solid-state component was washed by n-heptane.

[0123] Subsequently, n-heptane 50ml refined like the above was introduced into the flask which fully carried out the nitrogen purge, and 0.24 mols of solid-state components compounded above were introduced by Mg atom conversion. Subsequently, the SiCl₄ 0.4 mol was mixed to n-heptane 25ml, and it introduced to the flask in 30 degrees C and 30 minutes, and was made to react at 70 degrees C for 3 hours. It washed by n-heptane after reaction termination. Subsequently, 0.024 mols of phthalic-acid chloride were mixed to n-heptane 25ml, and it introduced to the flask in 70 degrees C and 30 minutes, and was made to react at 90 degrees C for 1 hour.

[0124] It washed by n-heptane after reaction termination. Subsequently, SiCl₄ 20ml was introduced and it was made to react at 80 degrees C for 6 hours. It fully washed by n-heptane after reaction termination. The titanium content of this component was 1.21 % of the weight.

[0125] the component which introduced 50ml of fully refined n-heptanes into the flask which fully carried out the nitrogen purge, and was subsequently obtained above -- 5g introducing -- subsequently (CH₃) -- 3 CSi (CH₃) (OCH₃)₂ [a component (ii)] -- 1.6ml -- introducing -- subsequently -- TiCl₄ 0.52ml -- further -- triethylaluminum 3.0g It introduced, respectively and was made to contact at 30 degrees C for 2 hours. It washed enough by n-heptane after contact termination, and considered as the solid-state component (i). The titanium content in a solid-state component (i) was 3.64 % of the weight.

[0126] Content volume 1.5L which fully carried out the nitrogen purge It is n-butyl lithium 0.4g as a component (ii) after introducing into a churning type autoclave n-heptane 400ml dehydrated

and deoxidized and cooling the inside of a system at 15 degrees C. And above-mentioned solid-state (component i) 4g It introduced, feed of the propylene was carried out by 8g/hr for 0.5 hours, and precuring was performed. The residual-pressure polymerization was performed for 10 minutes after propylene feed termination. It washed twice by n-heptane after termination, and the target catalyst component for polymerizations was obtained. 4g of this catalyst component for polymerizations Upwards, a polymer is 3.72g. A **** and the solid-state catalyst component for polymerizations (i) are 7.72g. It was obtained.

[0127] (2) Manufacture inner capacity 10L of a copolymer n-heptane 2.5L after a propylene permutes an autoclave It teaches and is triethylaluminum 2.5g. And above-mentioned solid-state catalyst (component i) 0.4g It introduced into the bottom of a propylene ambient atmosphere.

[0128] Subsequently, the propylene was pressed fit agitating and it held for 10 minutes to 65 degrees C and 0.5kg/cm2G. Then, the charge of 1 and 9-deca diene was started and pressurization maintenance was carried out with the propylene at 2.0kg/cm2G at coincidence. 1 and 9-deca diene is 350 ml/hr. It inserted in for 2 hours. In addition, just before introducing the solid-state catalyst component (i), the time [from] of polymerization termination held the hydrogen concentration of the autoclave gaseous-phase section to 4.0 volume %. After inactivating a catalyst by the 5 hours after n-butanol, catalyst residue was extracted with water, centrifugal separation recovered the copolymer, and it dried.

[0129] The obtained copolymer (henceforth "Resin E") powder was 2.1kg, and bulk density was 0.51g/cc. As a result of GPC measurement, Mn was 56,000 and Mw was 350,000. Again The content of 1 and 9-deca diene in which copolymerization was carried out by analysis by 1 H-NMR was 0.33-mol %.

[0130] an example 1 -- 200ml flask which fully carried out the nitrogen purge -- resin C 1.3g and resin A Xylene 40ml fully dehydrated and deoxidized 1.3g and poly methylhydrogensiloxane (Shin-Etsu Chemical [Co., Ltd.] make trade name: KF99) 0.025g And platinum / divinyl tetramethyl disiloxane (Shin-Etsu Chemical Co., Ltd. make, trade name-L50T) 0.014g It put in and was made to react at 160 degrees C under nitrogen-gas-atmosphere mind for 144 hours.

[0131] Then, methanol 500ml is filled with a reaction solution, - desiccation classified by ** of the precipitating block copolymer is done, and it is 2.5g. It obtained.

[0132] 2g of this block copolymer - desiccation classified by ** of the block copolymer which added to methyl-ethyl-ketone 500ml, and precipitated to xylene 100ml after carrying out the heating dissolution was done. the collected block copolymer -- 1.9g it is -- the styrene content was 49.0 % of the weight by the infrared spectral-analysis method. This thing was Mn25,000 and Mw51,000 as a result of GPC measurement.

[0133] It sets in the example 2 example 1, and is Resin C. 0.65g, resin A 1.95g Except having changed, it carries out like this example and is 2.4g of block copolymers. It obtained.

[0134] the block copolymer collected as a result of performing purification processing and analysis like an example 1 -- 1.8g it is -- the styrene content was 60 % of the weight. Moreover, it was Mn29,000 and Mw66,000.

[0135] Except having changed Resin C to Resin D, and having changed Resin A to Resin B in example 3 example 1, it carries out like this example and is 2.5g of block copolymers. It collected.

[0136] the block copolymer collected as a result of performing purification processing and analysis like an example 1 -- 1.5g it is -- the styrene content was 31.1 % of the weight. Moreover, it was Mn53,600 and Mw108,000.

[0137] Except having changed Resin C to Resin E in example 4 example 1, it carries out like this

example and is 2.5g of block copolymers. It collected.

[0138] the block copolymer collected as a result of performing purification processing and analysis like an example 1 -- 1.7g it is -- the styrene content was 38.8 % of the weight.

Moreover, it was Mn63,000 and Mw360,000.

[0139] the example 1 of a comparison -- the inside of the round bottom flask which fully carried out the nitrogen purge -- resin C5g After having put in 200ml of carbon tetrachlorides, carrying out the temperature up to 70 degrees C and agitating for 30 minutes at this temperature, it cooled to the room temperature under churning. It is 0.18g of bromines there. After making it react for 1 hour, the temperature up was carried out to 60 degrees C, and it was made to react further for 30 minutes in addition.

[0140] Subsequently, it is methanol 2L about contents in a flask. It agitated [be / it / under adding] for 1 hour, and suction filtration was carried out and the solid-state product was carried out the ** exception. Furthermore, after repeating actuation of adding a solid-state product to a methanol and filtering it, 4 times, a solid-state product is dried, and it is 4.98g. The bromination polymer was obtained. As a result of measuring a bromine content with ion chromatography, it was 3.3 % of the weight.

[0141] In the flask, styrene 6.7g and xylene 115ml were added, n-butyl lithium 49mg was added there, and the living poly styryl anion was compounded.

[0142] It is the 1.0g of the above-mentioned bromination polymers into another flask. It put in, xylene 120ml was added and it agitated at 50 degrees C. Said living poly styryl anion is added there, and it agitated for 144 hours and was made to react at 50 degrees C.

[0143] Subsequently, this was poured in and settled into the methanol of an overlarge, and solid-state products were collected and it dried. After making 1,4-dioxane carry out the **** dissolution of this solid-state product for 2 hours and leaving it at 20 degrees C of night, the insoluble sections were collected the ** exception and it dried.

[0144] the obtained polymer -- 1.01g it is -- when the content of polystyrene was calculated from the infrared absorption spectrum, it was 6.5 % of the weight. Moreover, as a result of measuring a bromine content with ion chromatography, it was 1.5 % of the weight.

[0145] the block copolymer obtained in an application 1 and the two examples 1, polypropylene (Mitsubishi Petrochemical Co., Ltd. make; trade name "MA8"), and Pori (2, the 6-dimethyl -1, 4-phenylene ether) (Japanese polyether company make --) Intrinsic viscosity measured in the chloroform in 30 degrees C: Use the PURASUTO mill (Oriental energy machine factory company make) of 60ml of content volume by the presentation shown in Table 1 by making 0.4 dl/g into an application 1, and they are for 5 minutes and rotational frequency 180rpm at 230 degrees C. Melting kneading was carried out. The following estimated physical properties for the obtained resin constituent, and the result was shown in Table 1. It was similarly shown in Table 1 by making into an application 2 (comparison) the case where a block copolymer is not used.

[0146] (1) Carry out cutting of the test piece with a bending elastic-modulus width of face [of 25mm], and a die length of 80mm, and it is JIS. K Based on 7203, it measured using the Instron testing machine.

[0147] (2) Injection molding of the test piece with Izod-impactive-strength die length of 31.5mm, a width of face [of 6.2mm], and a thickness of 3.2mm was carried out, and Izod impactive strength with a notch was measured using the Izod impact tester (minimax CSmade from custom-made science tee FIKKU- 138TI molds).

[0148]

[Table 1]

表 1

		応 用 例	
		1	2 (比較)
配合組成 (重量部)	ポリプロピレン (MAB)	50	50
	ポリ (2, 6-ジメチル-1, 4-フェニレンエーテル)	50	50
	ブロック共重合体 (実施例 1)	20	0
評価結果	アイゾット衝撃強度 ($\text{kg}\cdot\text{cm}/\text{cm}^2$)	6.5	2.1
	曲げ弾性率 (kg/cm^2)	13,000	13,000